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ANTIWEAR ADDITIVES, WEAR STUDIES ON CHEMICAL
ADDITION AGENTS FOR IMPARTING AN EFFECTIVE
LUBRICATING RESPONSE IN POLYSILOXANE
(SILICONE) FLUIDS

NAVAL AIR DEVELOPMENT CENTER,
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ANTIWEAR ADDITIVES

Wear Studies on Chemical Addition Agents for Imparting an Effective Lubricating Response in Polysiloxane (Silicone) Fluids

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Organic Phosphates	Antiwear Additives									
Chlorendate	Boundary Lubricants									
Thiadiazole	Surface Reactivity									
Pro-Wear	Four-Ball Wear Test Results									
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) <p>An additive package based on chlorendate and thiadiazole molecular structures has been discovered which imparts antiwear properties to tetrachlorophenyl-methyl siloxane fluids that have been previously unattainable. For the first time a polysiloxane based fluid possessing antiwear properties comparable to such outstanding lubricants as petroleum oils, synthetic hydrocarbons, diesters and phosphate esters was formulated. In addition, a detailed analysis of</p> <p>(Continued)</p>										

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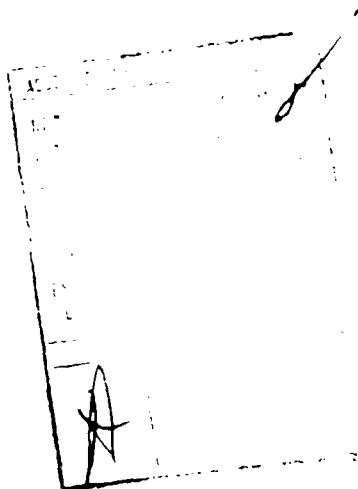
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the modification of friction surfaces (steel-on-steel) using organo-phosphate addition agents in polysiloxane fluids has refuted the commonly held belief that the inability of antiwear additives to function in polysiloxane media at low concentrations is due to the fact that the additive is substantially excluded from the surface. Evidence is presented to show that additive-surface interactions are indeed prevalent resulting in an antagonistic (pro-wear) action. In one specific instance depending on load and concentration a beneficial lubricating response is achieved with a tetrachlorophenylmethyl siloxane fluid containing alkyl-phosphate derivatives. The use of organo-phosphates as antiwear agents in polysiloxane has previously proved unfruitful, therefore, these results represent a significant area for further study.



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S U M M A R Y

INTRODUCTION

The use of chemical additives in lubricating oils to increase their effectiveness under extreme operating conditions is widely recognized. These additives are generally referred to as antiwear additives. Such additives usually consist of organo-sulfur, -chlorine or -phosphorus compounds or mixtures thereof although they are not limited to these chemical families. When added to the lubricating oil in quantities of one to two percent, catastrophic wear of mechanical components will be prevented under extreme operating conditions. The mechanism established for this beneficial action involves the controlled decomposition of the additive as a result of elevated temperatures caused by localized metal-to-metal contact at surface asperities. The additive reacts chemically with the freshly worn surface to form films of sulfides, chlorides or phosphate complexes which exhibit low shear strengths, thus making it possible for one surface to move over the other with least resistance.

For conventional petroleum base oils which are limited to lower temperature applications (275° to 300°F) the thermal stability of the antiwear additive usually coincides with the thermal stability of the base oil. In recent years a number of synthetic fluids have been developed with temperature stabilities well above the petroleum base oils (500° to 600°F). One such class of materials is the polysiloxanes or more commonly called silicone fluids. It was found that the commonly used antiwear additives for petroleum base oils were completely ineffective in the silicone oils. Under a previous NAVAIRDEVCON (Naval Air Development Center) Independent Research Program the first suitable antiwear additive based on thiadiazole chemistry was developed and patented for imparting effective lubricating properties to silicone fluids. However, the upper temperature stability of this additive was limited to 250° to 275°F, well below the useful temperature range of silicone fluids. Consequently there exists a need to broaden the range of chemical additives suitable for use in silicone fluids and also to take advantage of the higher temperature capabilities so that new military weapons systems can be designed for optimum performance and reliability.

The work reported herein was conducted under Independent Research Task Area No. ZR01302, Work Unit No. GC131.

RESULTS

1. A polysiloxane formulation containing 2 weight percent dibutylchlorosulfate and 0.25 weight percent 2,5-bis-t-dodecyl dithio-1,3,4 thiadiazole in tetrachlorophenylmethyl siloxane fluid has been discovered which possesses antiwear properties previously unattainable with polysiloxane fluids. In fact the boundary lubricating properties of this formulation are comparable to those of formulated petroleum oils, synthetic hydrocarbons, diesters and phosphate ester fluids. A patent application covering this unique discovery has been filed.

2. An investigation of the friction surface (steel-on-steel) modification effects of organo-phosphates in polysiloxane media has refuted the belief that such additives are essentially excluded from the surface at low concentrations. It has been shown that these additives in most cases have an antagonistic effect i.e. increase wear rates at low concentrations.

3. The use of organo-phosphates as antiwear agents in polysiloxane fluids has previously proved unfruitful. As a result of this study a polysiloxane formulation containing 4 to 5 weight percent of an alkyl-phosphate in tetrachlorophenylmethyl siloxane exhibited improved antiwear properties under high load conditions.

CONCLUSIONS

1. Polysiloxane fluids possessing antiwear qualities comparable to conventional lubricating media can be achieved through the use of chemical addition agents in minor concentrations.

2. Having overcome the disadvantage of poor boundary lubricating properties associated with polysiloxanes, these fluids may now be considered for applications where their more desirable properties such as high temperature stability, oxidation resistance, low volatility, etc. can be used to greater advantage.

FUTURE WORK

Although the use of selected chemical addition agents in polysiloxane fluids has proved beneficial in eliciting a pronounced boundary lubricating effect, the exact nature of their action is still unknown. A better understanding of the mechanism by which these additives function will provide guidelines for the development of a new generation of military aircraft lubricants and fluids. Having established basic property relationships, effort will continue toward:

1. Identifying the chemical nature of surface reaction products resulting from antiwear activity.
2. Determining plausible mechanisms based on chemical reactivity.
3. Establishing molecular composition and structure for optimum antiwear functionality.
4. Synthesizing chemical addition agents based on the above findings.
5. Establishing performance characteristics at elevated temperatures and loads on selected polysiloxane formulations.

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BACKGROUND

SURFACE CONSIDERATIONS

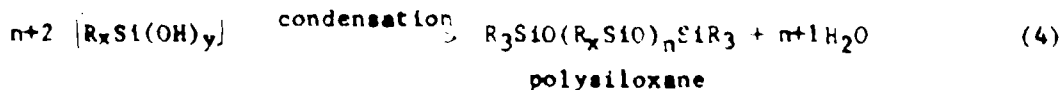
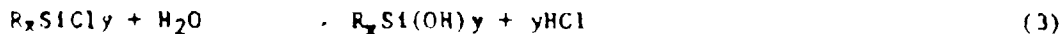
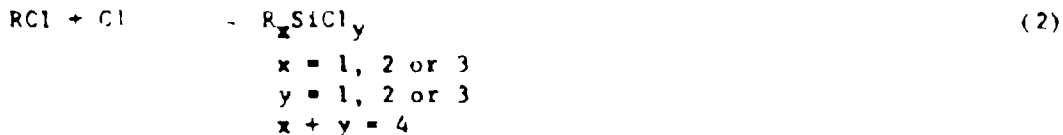
A schematic representation of typical friction surfaces is shown in Figure 1. Under hydrodynamic conditions of lubrication, the two surfaces are separated by a thin oil film and ideally no wear occurs. However, with increased load the thickness of the oil film diminishes to the point where surface contact occurs. This regime is generally referred to as boundary lubrication conditions. As depicted in Figure 1, the topography of such surfaces essentially consists of a series of "hills" and "valleys" (asperities) which exist even for highly polished surfaces. When surface contact is made at the asperities, adhesive interactions result in increased generation of heat and the formation of wear particles. Because the points of contact are microscopic in nature, the total load is carried by only a very small fraction of the actual surface area. All of these conditions combine to produce wear in mechanical components.

An effective means of preventing or alleviating this condition involves the addition of chemical species to the oil in minor concentrations (usually less than 2 percent). The temperature generated at asperity contacts can exceed 2000°F although for only a fraction of a second. The additive reacts with this "hot spot" to form a new chemical compound on the surface which has a lower shear strength than the base metal and thus the surfaces move relative to one another with lower resistance. At bulk fluid temperatures (less than 300°F) the additive is stable enough to resist decomposition.

The general classes of additives used for this purpose are sulfur, chlorine or phosphorus containing organic compounds while the resultant surface reaction products have been identified as inorganic metal sulfides, chlorides, phosphate or phosphate complexes.

SILICONE CHEMISTRY AND PROPERTIES

The preparation of polysiloxanes can be represented by the following series of reactions:



Essentially silicone polymers contain repeating Si-O linkages making their "backbone" completely inorganic while various organic substituents are attached to the Si atoms. Some of the more common forms of polysiloxane polymers are presented in Figure 2.

In general the properties of polysiloxane fluids which are substantially different from conventional lubricating media and which affect their lubricating ability include:

1. Free rotation of the structural units relative to the siloxane bonds together with low inter-molecular interaction make formation of compact oriented structures between two surfaces under load difficult (39).
2. Siloxane bonds are partially ionic in nature and therefore highly reactive in heterolytic type reactions. Antiwear additives function through homolytic (free radical) type reactions which do not readily occur in heterolytic systems (39).
3. With the exception of phenylmethyl silicones the conventional antiwear additives are only slightly soluble in silicone fluids.

"STATE-OF-THE-ART" REVIEW

The literature abounds with information concerning the use of antiwear additives and the nature of action in conventional (hydrocarbon) lubricating fluids. On the contrary, the scarcity of this type of information relevant to polysiloxane fluids is conspicuous.

Conventional Lubricating Media

The first use of antiwear additives occurred in the mid-1920's in order to permit operation of hypoid gears. These first compounds, many of which are still employed today, contained sulfur, chlorine or phosphorous atoms in their molecular structures. Since that time the application of antiwear additives has spread to many other mechanical components. They were believed to function by forming a film of low shear strength such as a sulfide, chloride or phosphide as discussed previously. By repeated shear breakdown and reformation, the film prevented seizure of metal surfaces. A large number of investigations seemed to support this belief (1-11).

In 1940 Beeck, Givens and Williams (5) postulated that the effectiveness of phosphorous containing additives such as tricresyl phosphate was due to the formation of an iron-iron phosphide eutectic of low melting point at the asperities which chemically "polished" the surface. In 1954 Klaus and Fenske (12) found that the low wear was not accompanied by any gross smoothing or "polishing" of bearing surfaces. This was also confirmed by Furey (13) in 1963. In 1965 three papers appeared which refuted the iron-iron phosphide eutectic formation theory. Barcroft and Daniel (14) using radioactive triphenyl phosphate showed that this additive formed films of metal phosphates and metal organo phosphates. It was suggested that the neutral phosphate ester adsorbs on the metal surface, then decomposes in the contact area to give the acid phosphate which reacts with the metal surface to form metal organic phosphate. This then decomposes to form the metal phosphate. Godfrey (15) identified iron phosphates on sliding surfaces lubricated with tricresyl phosphate. No evidence of iron phosphide could be found in either of the above studies. Klaus and Bieber (16) using radioactive tricresyl phosphate identified iron phosphates on bearing surfaces and attributed their formation to polar impurities in tricresyl phosphate. In 1968 Bieber, Klaus and Tewksbury (17) using tricresyl phosphate

showed that the antiwear behavior in a formulated lubricant appeared to be due to the acid phosphate and not the tricresyl phosphate. The tricresyl phosphate acted as a reservoir for the formation of acid phosphate during the life of the lubricant. In 1970 Goldblatt and Appeldoorn (18) showed evidence contrary to Bieber, Klaus and Tewksbury (17) that tricresyl phosphate and other phosphate and phosphite esters act as antiwear agents by directly reacting with metal surfaces. No prior hydrolysis to the acid phosphate appeared to be required. This was also confirmed in 1970 by Sakurai and Sato (19). From x-ray analysis they confirmed the presence of iron phosphates and a small amount of iron phosphide. They concluded from their results that the iron-iron phosphide eutectic scarcely contributed to the lubrication mechanism. In 1974 Forbes and Battersby (20) reported on the use of dialkyl phosphites as antiwear additives. They found that the phosphites were better antiwear agents than the corresponding phosphates and attributed the formation of both organo and inorgano phosphites to hydrolysis occurring in solution and at the surface.

In regard to sulfur containing antiwear additives, the initial theories assumed that the film formed on metal surfaces was the metallic sulfide. Indeed several papers (21-24) have indicated that with steel or iron surfaces, the iron sulfide is formed and it is this compound that is providing reduced wear. Godfrey (25) in 1962 analyzed, by six methods, the films formed on steel surfaces from mineral oil saturated with elemental sulfur. The major component found was Fe_3O_4 with minor constituents of FeS and FeO . The sulfides were believed to promote the oxidation of iron, but the combination of both oxide and sulfide in the films were necessary for high load capacity. Still others have found no evidence of the formation of iron sulfide. Buckley (26) in 1974 using Auger Spectroscopy found that sulfide films on iron surfaces are displaced by oxygen. In 1976 Baldwin (27) using x-ray photoelectron spectroscopy identified metallic sulfide compounds on surfaces which provided effective boundary lubrication.

With regard to chlorine containing additives, again the obvious postulations were that a metallic chloride was formed on the bearing surface. Analyses of iron containing bearing surfaces have shown that FeCl_3 and FeCl_2 are present as well as the unexpected oxychlorides (28).

Polysiloxane Lubricating Media

As previously indicated the types and magnitudes of studies performed on conventional lubricating fluids far exceed those which have been performed on polysiloxane fluids. The commercial availability of silicone fluids occurred only about 30 years ago. This and the lack of solubility of conventional types of antiwear additives in dimethyl siloxane fluids are the basic reasons for the limited availability of technical information in the area of additive interactions.

It was evident from the early work of Zisman (29) in 1946 and Currie (30) in 1950 that the application of silicones as lubricants would be limited because of their poor lubricating qualities for the most common bearing - metal combination; namely, steel-on-steel. Because of the many desirable properties of silicone fluids, efforts were then directed toward overcoming this drawback. Although these efforts were hampered by the poor solubility of most materials in silicones, Murray and Johnson (31) in 1952 found that incorporating 30 percent of a diester improved the lubricating properties but such a blend offered only

a compromise of the properties of the two fluid types. In the early to mid 1950's Fletcher, Hunter (32) and Brown (33) improved the lubricating properties of silicones by an alternate route. They incorporated an active antiwear element from the halogen family into the polymer chain. The halophenyl group offered improved lubricity for ferrous metals while retaining the inherent stability of the siloxane polymer. Another chemical modification was based on the substitution of dimethyl groups with trifluoropropyl methyl groups. Schiefer and Van Dyke (34) in 1963 reported on the improved boundary lubricating properties of these fluoroalkyl silicones in bench and pump tests. Also, introduction of alkyl groups in the silicone polymer was found to have a beneficial effect on the lubricating properties, however the improvement obtained was at the expense of the inherent stability of the siloxane chain (35). In 1968 the approach toward providing enhanced lubricating properties for siloxane fluids reverted to chemical addition agents. Devine and Lamson (36) were issued a patent based on the improvement obtained using polysulfides and thiadiazoles in siloxane fluids. In 1973 Groenhof and Swihart (37) were issued a patent on the use of chlorandates as lubricity additives for silicone fluids. In 1974 Groenhof and Quaal (38) reported on the fact that the use of conventional antiwear additives were effective in phenylmethyl siloxane fluids although at higher concentrations than normally used. In 1965 Vinogradov, Nametkin and Nossov (39) reported on the fact that additives which were highly active in preventing steel seizure in hydrocarbon media are either completely inactive in polysiloxanes (methylphenyl siloxanes) or are much less active (ethyl siloxanes). Their hypothesis attributes this to the absence of processes involving chain reactions initiated by free radicals in polysiloxanes.

The work described above covering siloxane fluids was aimed mostly at improving lubricating performance in contrast to work reported with conventional fluids where the major emphasis has been on determining what chemical species is formed on the surface and by what mechanism it is formed. In general, all of the improvements still fell short of the beneficial lubricating properties exhibited by compounded petroleum or hydrocarbon lubricants.

EXPERIMENTAL

The Shell four-ball wear test apparatus was employed throughout this investigation. The apparatus has been adequately described elsewhere in the literature (40-41). Briefly described this test utilizes three balls locked immovably by a conical ring thereby forming a three point contact for a fourth ball held rigidly at the end of a drive shaft. The fourth ball rotates, under load, against the three stationary balls, all of which are immersed in the lubricant under test. Ideally, circular wear scars are produced on the surface of the three stationary balls and the degree of wear is expressed as the average diameter of these scars. The smaller the wear scar, the better the lubricating characteristics of the fluid under test. Test conditions which remained constant throughout this investigation are as follows:

- a. Metal Specimens: AISI 52100 steel balls
- b. Test Time: 1 hour
- c. Speed: 1200 RPM

Load ranges studied included 10, 20 and 40 kg. All of the curves presented show data generated at 167°F. Some data presented in tabular form was generated

at 350°F. The wear scar diameters reported are in millimeter units and where critical points were established are the average of several separate determinations.

All of the polysiloxane fluids and chemical additives were obtained from commercial sources. The dichlorophenylmethyl fluid is no longer commercially available. All materials were used as received.

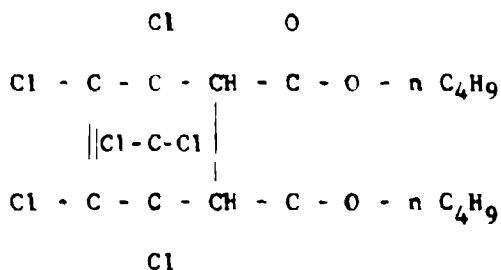
R E S U L T S

ANTIWEAR ADDITIVES FOR TETRACHLOROPHENYLMETHYL SILOXANE FLUID

A literature search in the area of antiwear additives for siloxane fluids in general indicated the need to establish fundamental performance characteristics in regard to antiwear properties. Our initial efforts in this phase of the investigation led to the discovery of a tetrachlorophenylmethyl siloxane lubricant composition (42) which possessed antiwear qualities previously unattainable with silicone fluids. Table I lists the four-ball wear test results obtained for various siloxane/additive formulations. The chemical structures of the additives employed are given below:



2,5-bis-t-dodecyl dithio-1,3,4 thiadiazole



dibutylchlorendate

Each additive was investigated individually and in combination at several concentration levels. Both the thiadiazole and the chlorendate are observed to improve the antiwear properties of the base silicone fluid at relatively low concentrations (formulation Nos. 2 and 6, respectively). It was of interest to determine whether a further improvement in antiwear properties could be observed with a combination of additives (synergistic effect). A remarkably low wear scar diameter was obtained with 2.0 weight percent chlorendate and 0.25 weight percent thiadiazole in the silicone base fluid (formulation No. 11). The antiwear properties of this formulation are comparable with those of petroleum fluids, synthetic hydrocarbon and phosphate ester fluids under the same test conditions, as shown in Table II. In addition the antiwear properties of formulation 11 are maintained even at temperatures as high as 350°F (Table III).

These results are specific for the tetrachlorophenylmethyl siloxane fluid. Other siloxane fluids such as dimethyl and phenylmethyl do not respond to the chlorendate/thiadiazole additive package in a like manner. A dichlorophenylmethyl siloxane exhibits improved antiwear properties (0.80 mm wear scar diameter) but at a concentration of 10 weight percent chlorendate and 1 weight percent thiadiazole.

ORGANO-PHOSPHATES AS ANTIWEAR ADDITIVES IN POLYSILOXANE FLUIDS

The action of organo-phosphates such as tricresyl phosphate in conventional lubricating media is well established. Therefore, our initial studies were concerned with establishing basic performance criteria of this type of antiwear agent in polysiloxane fluids. For this purpose four different phosphate compounds were selected, i.e. trioctyl phosphate (TOP), tributyl phosphate (TBP), tri-ortho-tolyl phosphate (TOTP) and tricresyl phosphate (TCP). TOTP is a specific isomeric form of TCP. Commercial TCP is a mixture of the ortho, meta and para isomers of tricresyl phosphate. Also, three different classes of polysiloxane fluids; i.e., the dimethyl, the phenylmethyl and the chlorophenylmethyl fluids were used as base stocks.

Dimethyl Siloxane

The results obtained on the four-ball wear analysis of the various phosphates in dimethyl siloxane fluid are graphically presented in Figures 3 through 11. The basic data generated can be found in Figures 3, 4 and 9. Figures 5 through 8 show the effect of load on wear and Figures 10 and 11 show the effect of viscosity on wear for the various phosphate compounds.

1. 50 cs Fluid at 20 Kg Load (Figure 3)

From the outset the addition of organo-phosphates exhibits a deleterious effect on the boundary lubricating properties of the base fluid. This is in contrast to the antiwear characteristics produced with these additives in hydrocarbon fluids. In this context the organo-phosphates can be considered to act as "pro-wear" additives as opposed to antiwear additives. In each instance a concentration is reached where a maximum wear scar is produced. On continued increase of additive concentration the wear scar decreases toward the inherent boundary lubricating properties of the particular organo-phosphate. Table IV quantifies major characteristic wear scar data points based on molal (moles of additive, per 1000 grams of siloxane) quantities of phosphate additive. Three data points were selected to characterize each phosphate compound with respect to molal concentration which will result in:

- the maximum wear scar,
- the wear scar equal to that of the 100 percent siloxane, and
- the wear scar equal to that produced with 100 percent additive.

The order of increasing molal concentration of additive exhibiting

- a maximum wear scar is $TCP < TOP < TOTP < TBP$,
- wear scar equal to that for 100% siloxane is $TOP = TOTP = TCP < TBP$, and
- wear scar equal to that for 100% additive is $TOTP < TCP < TOP < TBP$.

The most striking difference occurs at the point where the concentration of additive is such that the quantity of silicone present has no effect on the inherent antiwear properties of the particular additive. For TCP and TOTP this occurs at a relatively low concentration (2.7 and 1.8 molal, respectively) while with the TOP and TBP it occurs at a much greater concentration (6.9 and > 11.3 molal, respectively).

2. 50 cc Fluid at 40 Kg Load (Figure 4)

At this higher load only the TOTP and to a lesser extent TCP effect an increase in wear scar at the initial lower concentrations. TOP and TBP exhibit a slight antiwear effect which eventually is destroyed on increased addition of additive to the point where a maximum wear scar is again produced. After each maximum wear scar the wear scar decreases toward that produced with pure additive. Table V quantifies the characteristic points on the curves. The order of increasing molal concentration of additive exhibiting:

- a. a maximum wear scar is TCP-TOTP, TOP < TBP,
- b. wear scar equal to 100% siloxane is TCP < TOTP < TOP < TBP, and
- c. wear scar equal to 100% additive is TCP-TOTP < TOP < TBP.

Again the most striking difference occurs at the point where the quantity of silicone present has no effect on the inherent antiwear properties of the particular additive. TCP and TOTP exhibit this property at 2.7 molal concentration while TOP is > 6.9 molal and TBP > 11.3 molal.

3. 10cc Fluid at 20 Kg Load (Figure 9)

The activity of TBP and TCP in 10 cc dimethyl siloxane at 20 Kg load is shown in Figure 9. The wear scar produced with TBP remains relatively constant to about 50 weight percent TBP after which it gradually decreases towards that of the pure phosphate compound. TCP exhibits a marked increase in wear scar diameter up to 5 weight percent, remains relatively constant to 60 weight percent then rapidly decreases toward that of the pure material at a 75 weight percent concentration.

Figure 10 compares the four ball wear results obtained with TBP in both 50cc and 10cc fluid. Essentially the curves are similar indicating no effect of viscosity on the wear scar diameters in the 50cc to 10cc range. On the contrary TCP (Figure 11) shows a marked difference in activity between the 10cc and 50cc dimethyl siloxane fluids.

4. 10cc Fluid at 40 Kg Load

Data points at this load level could not be obtained with the 10cc base fluid. Excessive wear resulting in severe mechanical vibration of the test apparatus prohibited a meaningful evaluation.

Phenylmethyl Siloxane

1. At 20 Kg Load (Figure 12)

The inherent lubricity of this fluid is so poor that wear scar diameters above 3.0mm are produced with no additive present. The addition of TBP, TOTP or TCP decreases the wear scar, TBP more rapidly than TOTP or TCP.

2. At 10 Kg Load (Figure 13)

At this lower load TBP reduces the wear scar diameter at a much lower concentration. The same is true for TCP but the effect is not as pronounced as with TBP.

Chlorophenylmethyl Siloxane

1. Dichlorophenylmethyl Siloxane at 20 Kg Load (Figure 16)

The addition of TBP or TCP to this base fluid resulted in an increased wear scar diameter throughout most of the concentration range with no sharp decrease in wear scar diameter at a specific concentration. The maximum wear scar diameter covered a broad range of concentrations for TBP (20 weight percent to 50 weight percent) while it was more specific for TCP (20 weight percent).

2. Dichlorophenylmethyl Siloxane at 40 Kg Load (Figure 17)

With TBP or TOTP at low concentrations (less than 20 weight percent) the wear scar increases rapidly to a maximum and then sharply decreases in the 20 to 40 weight percent range toward that obtained with the phosphate material alone.

3. Tetrachlorophenylmethyl Siloxane at 20 Kg Load (Figure 18)

The addition of TBP or TOTP increased the wear scar diameter at the low concentration range (less than 10 weight percent) with no sharp decrease from the maximum wear scar diameter with increasing concentration of phosphate additive.

4. Tetrachlorophenylmethyl Siloxane at 40 Kg Load (Figure 19)

In this base fluid the action of TOTP was rather unusual in that at concentration ranges of from 5 to 30 percent an irreproducible wear scar was observed. Thus in Figure 19 this portion of the graph is represented by a band depicting the range of wear scar diameters produced at a given concentration. As can be seen the amount of scatter is much greater than the repeatability generally observed for this wear test. With TBP a sharp decrease in wear scar diameter resulted followed by a gradual increase up to a concentration of 40 percent to a wear scar diameter which was maintained until a concentration of 80 percent additive was reached followed by decreasing wear scar diameters.

DISCUSSION

A comparison of the inherent boundary lubricating properties of the various polysiloxanes under consideration is shown in Table VI. The ability of each class to modify friction surfaces (steel-on-steel) is shown to vary considerably. All are poor or at best second-rate lubricating media compared to hydrocarbon lubricants. Vinogradov et al (39) have attributed these differences to the thermo-oxidative stability of the siloxane, with the lubricity lessening in the direction of the more thermally stable polymers.

The inadequacies of siloxane fluids for lubricating ferrous metals is considered to be due to the fact that the nature of the film formed on the bearing surface is such that it is not sufficiently condensed to provide load-carrying ability. In addition, the low bulk modulus (high compressibility) adversely affects the hydrodynamic component of lubricity.

The initial phase of this investigation has centered on the effect of organo-phosphates on the antiwear properties of polysiloxane media. In general with dimethyl siloxane the initial trend on the addition of phosphate additive is to increase wear scar size. If the phosphate additive does not get to the metal surface or is displaced by the siloxane as some authors (38) have proposed, the wear scar diameter produced should be the same as the siloxane with no additive present. As can be seen from Figures 3 and 4, this is clearly not the case. At low concentrations the phosphate additive is indeed altering the wear surface although in an antagonistic manner. With TOP and TBP at 40 Kg load there is a slight decrease in wear scar diameter at the outset but on increased additive concentration the wear scar rapidly becomes greater. What is evidenced on each curve is the fact that a synergistic effect in reverse is obtained. That is, concentrations are reached where the wear scar produced is greater than the wear scar diameters exhibited by either component individually. The combined reactivity of the siloxane and the phosphate with the ferrous surface under high loads and elevated "hot spot" temperatures produces a film which results in a wear rate higher than that exhibited by the individual components. Siloxanes are known to decompose, one the products being SiO_2 (Silica) which could react with iron oxide on the ferrous surface to form iron silicate. This, in conjunction with the iron phosphate or organo-iron phosphate film that is formed, may lead to the observed antagonistic behavior.

After a maximum wear scar is reached the wear scar of fluids with higher phosphate concentration diminishes toward that obtained with the particular phosphate alone. This occurs much more rapidly with the aryl phosphates than with the alkyl phosphates. The cause for this effect is not understood at this time.

The inherent boundary lubricating properties of the phenylmethyl siloxane is the poorest of the siloxanes studied. The severe wear condition that exists is not further aggravated on the addition of organo-phosphate. The same kind of surface reactions occurring in the dimethyl siloxane may also be found with the phenylmethyl siloxane but their characteristics are "masked" by the unusually high wear rate inherent with this base fluid. The alkyl phosphate (TBP) does provide friction surface modification at much lower concentrations than with the aryl phosphates (TCP, TOTP) as shown in Table VII. Since the phenylmethyl siloxane is more thermally stable, the formation of SiO_2 on the surface as previously proposed for the dimethyl siloxane will be more difficult thus allowing more complete formation of the phosphate film from TBP. It appears that the formation of such a film with TCP or TOTP is more difficult than with TBP in phenylmethyl siloxane fluids. However, with alkyl and aryl phosphates the antiwear properties for these formulations are extremely poor.

The addition of chlorine atoms to the phenyl groups in phenylmethyl siloxanes is shown to have a pronounced beneficial effect on the boundary

lubricating properties of the resultant chlorophenylmethyl siloxane. This effect is considered to be due to the formation of an iron chloride film on the friction surface. Two types of chlorophenylmethyl siloxane, one containing an average of two chlorine atoms per phenyl group, the other containing an average of four chlorine atoms were studied. Again it was shown that the organo-phosphate addition agent is reaching the surface at low concentrations as evidenced by the dramatic change in wear scar diameter. In most cases an antagonistic effect is observed. The exception occurred with TBP and TOTP in tetrachlorophenylmethyl siloxane at 40 Kg load. A significant decrease in wear scar diameter occurred in the 4 to 6 weight percent range using TBP which was not found in the dichloro fluid. The addition of TOTP also lowered the wear scar diameter but not to the same extent as TBP. In addition at given concentrations of TOTP in the 5 to 30 weight percent range repeatable wear scar diameters could not be produced. The reason for this effect is currently under study.

In order to further study the improved antiwear properties observed with TBP, other alkyl phosphates were investigated in both the dichloro and tetrachloro base fluids. Table VIII shows that with TOP and TRP (triethyl phosphate) similar results to TBP are obtained in both base fluids thus lending support to the fact that the results obtained are indeed representative of the difference between alkyl and aryl phosphates. These apparent differences have not been readily explained. An obvious difference is the chlorine content of the base fluids which may play an important role in the mechanism of additive action. Further analysis is required to account for the observed effects.

To date our analysis has demonstrated that polysiloxane lubricant compositions with vastly improved boundary lubricating properties are attainable. The specific mechanisms accountable for boundary lubricating action in polysiloxane media remain unknown. As noted in this discussion, hypotheses have been presented consistent with the experimental data to account for the observed effects. What is now required is a detailed analysis of the surface chemistry and reactivity of the friction surface as outlined in the "future work" statement in the summary section of this report, so that evidence may be obtained to support or dismiss current theoretical concepts. Toward this end the program is continuing.

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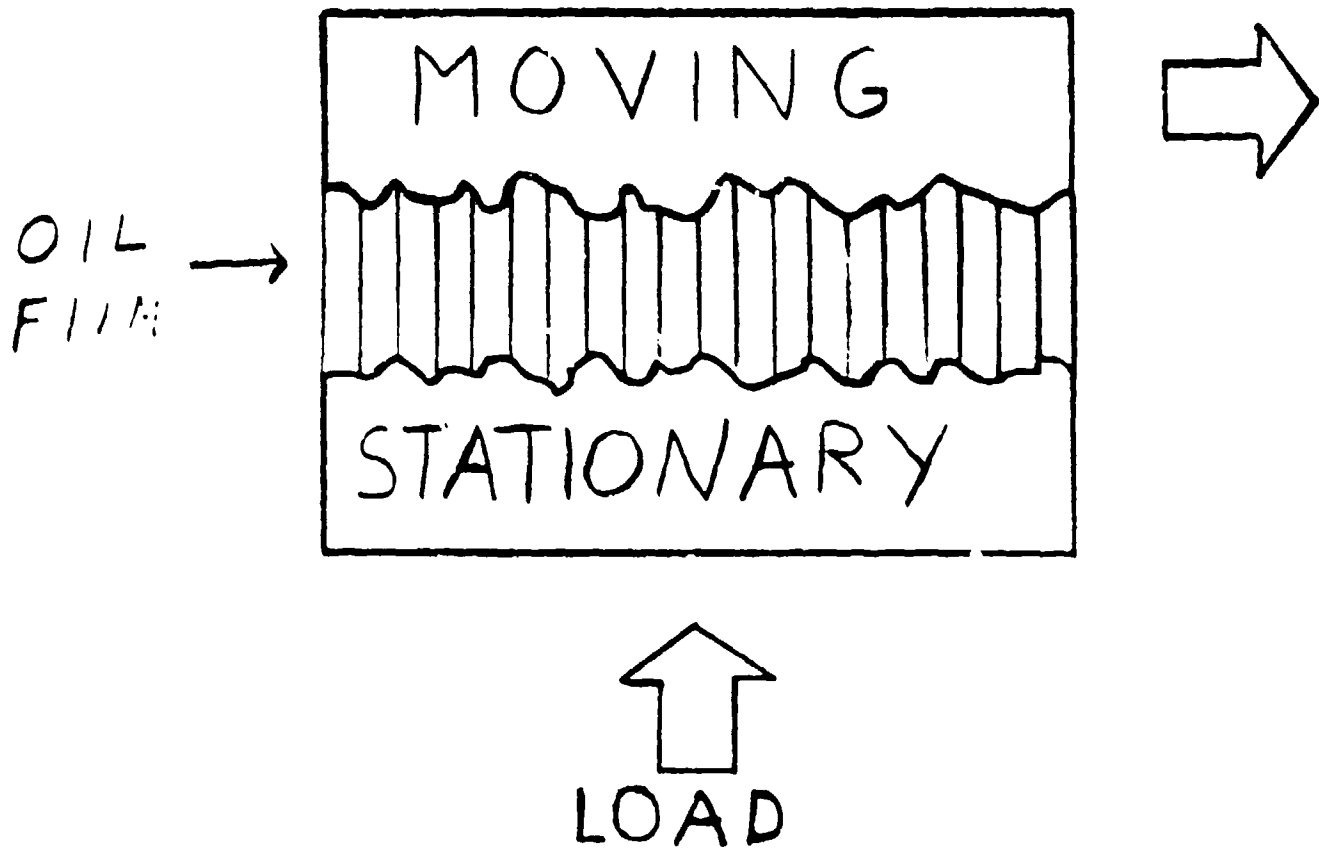
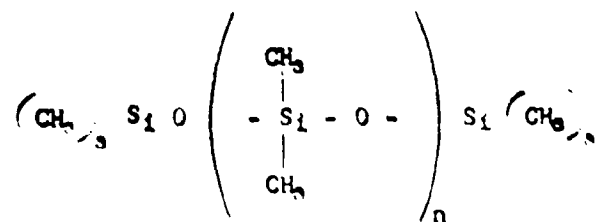
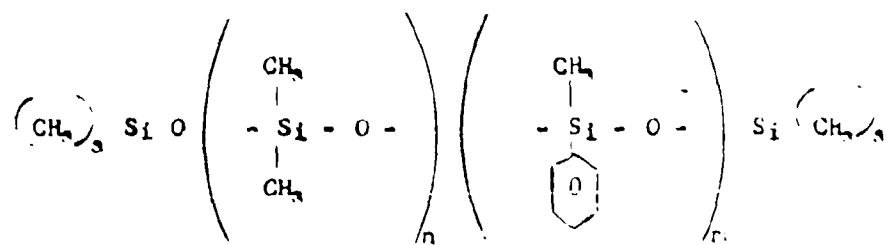


Figure 1. A Schematic Representation of Typical Friction Surfaces

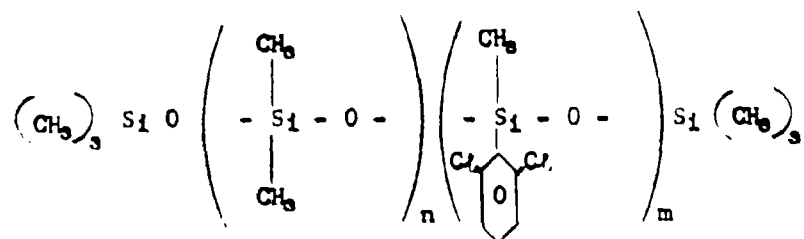


DIMETHYL SILOXANE

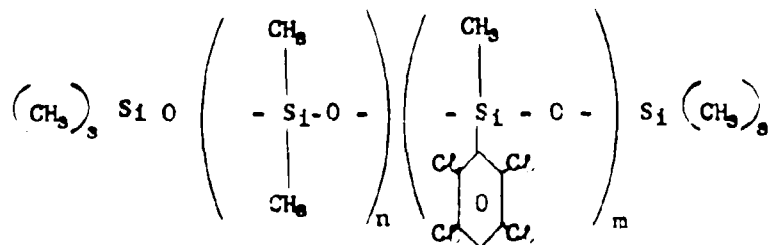


PHENYLMETHYL SILOXANE

Figure 2. Chemical Structure of Some Polysiloxane Polymers



DICHLOROPHENYLMETHYL SILOXANE



TETRACHLOROPHENYLMETHYL SILOXANE

Figure 2. Chemical Structure of Some Polysiloxane Polymers (Continued)

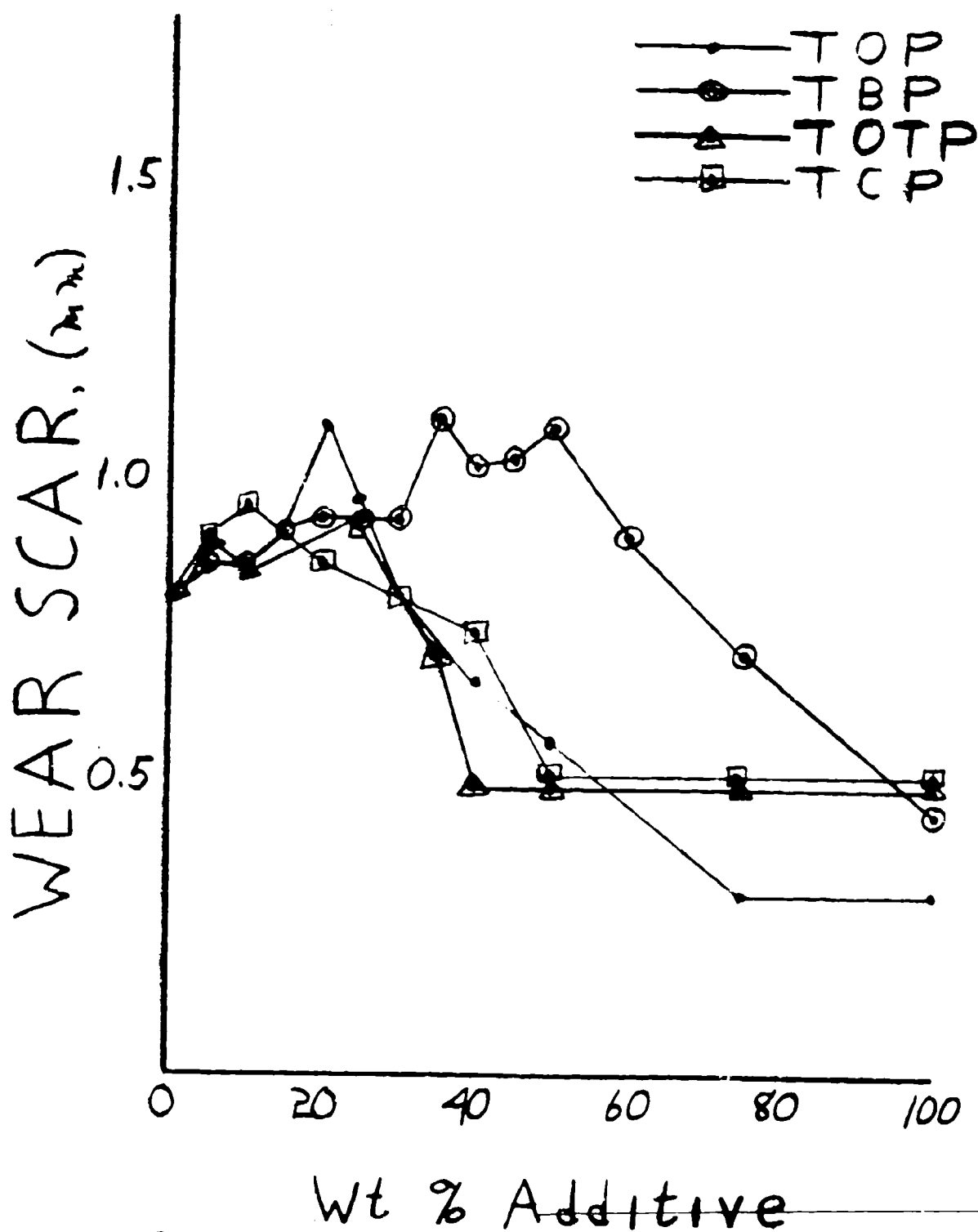


Figure 3. Four-Ball Wear Test Results on Dimethyl Siloxane Fluids (50 cs) with Various Phosphate Additives at 20 Kg Load

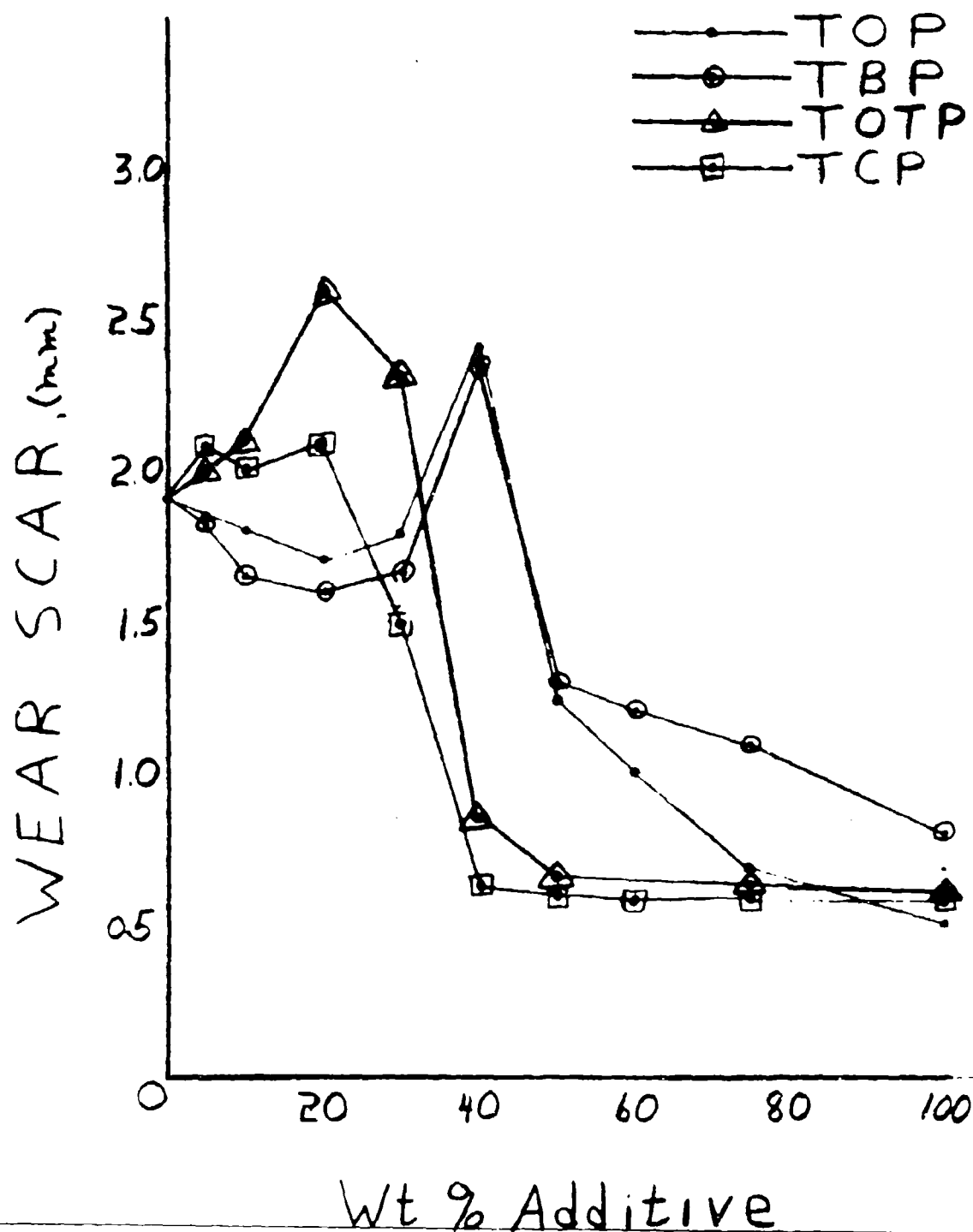


Figure 4. Four-Ball Wear Test Results on Dimethyl Siloxane Fluid (50 cs) with Various Phosphate Additives at 40 Kg Load

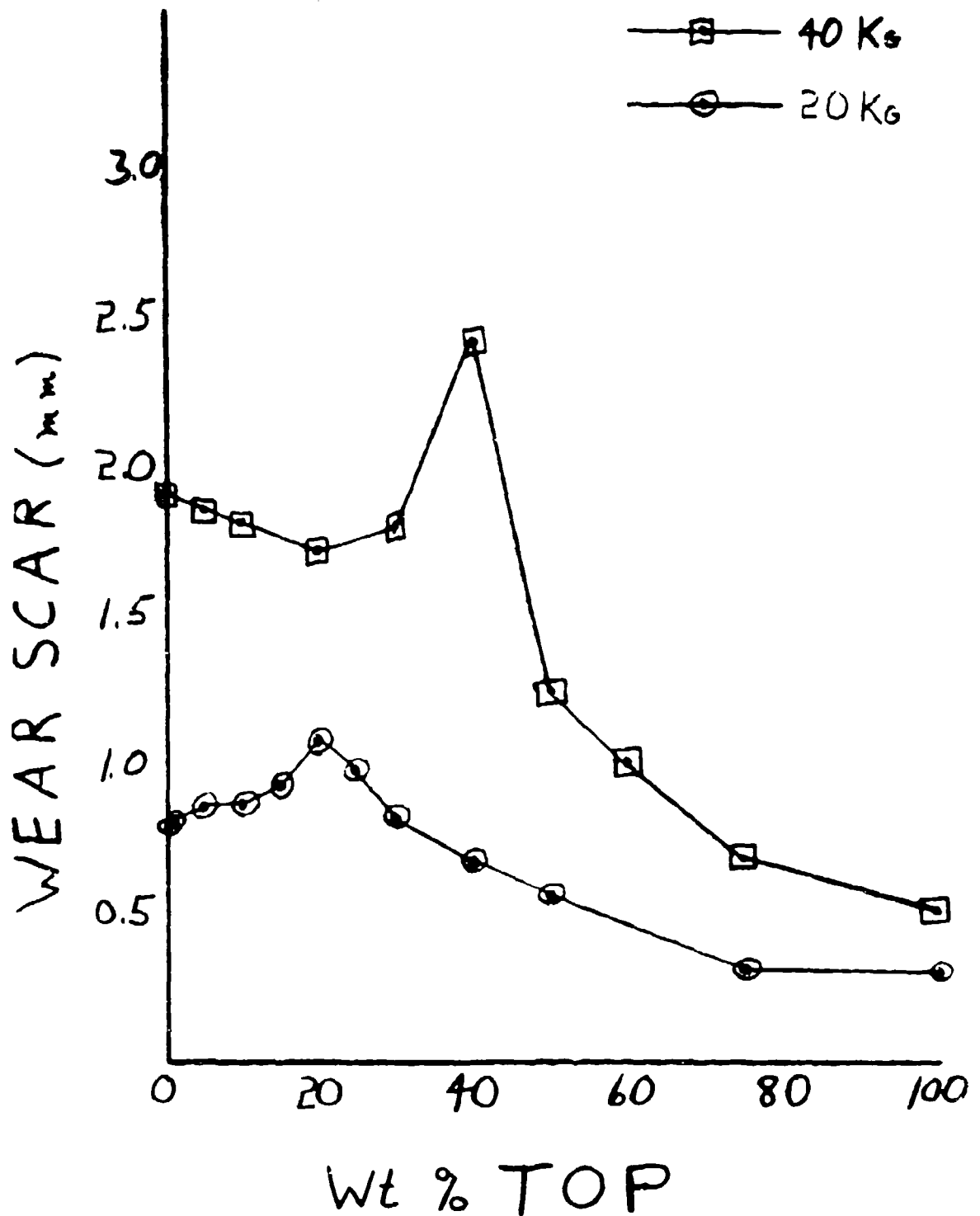


Figure 5. Four-Ball Wear Test Results on Dimethyl Siloxane Fluid (50 cs) with TOP at 20 and 40 Kg Load

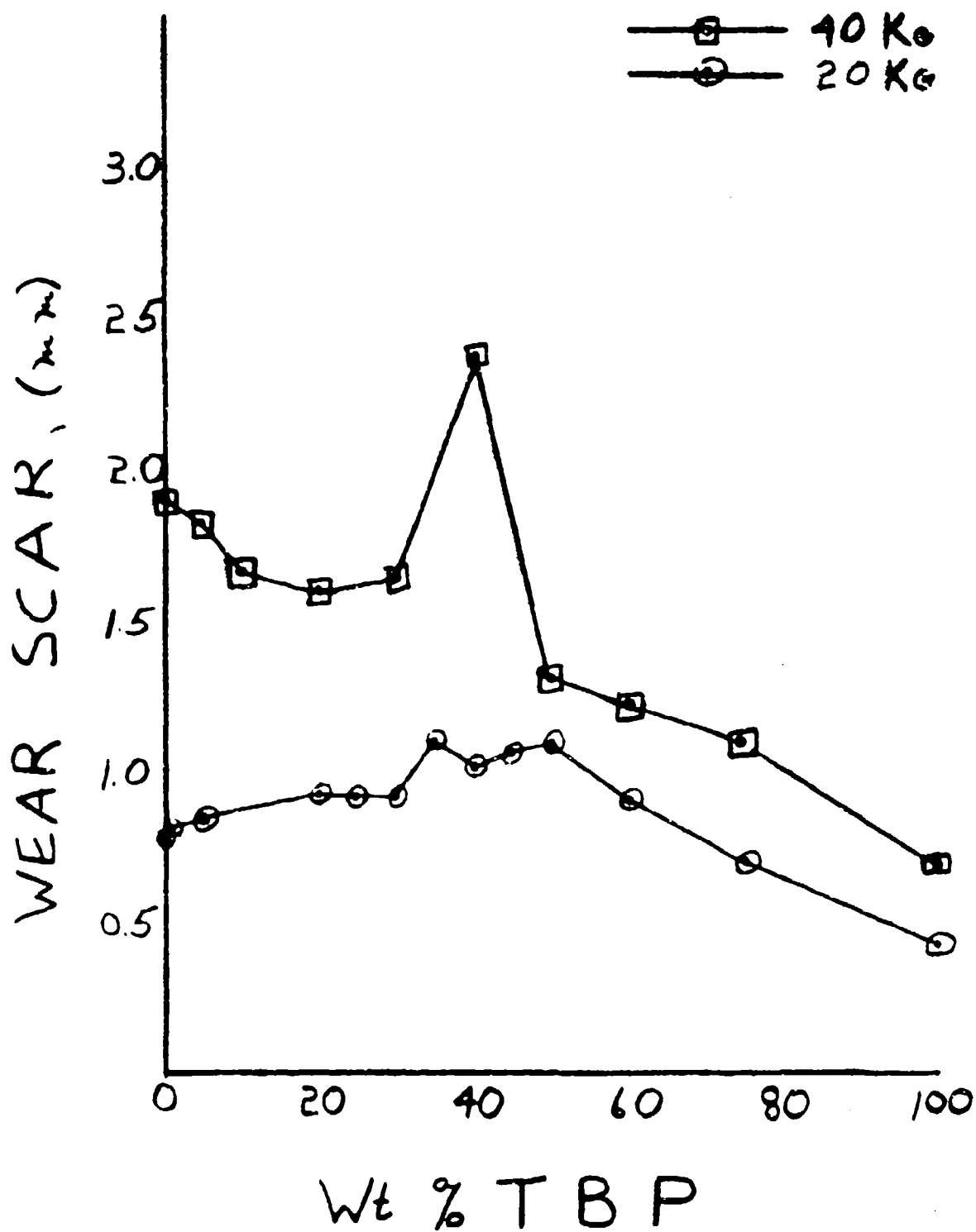


Figure 6. Four-Ball Wear Test Results on Dimethyl Siloxane Fluid (50 cs) with TBP at 20 and 40 Kg Load

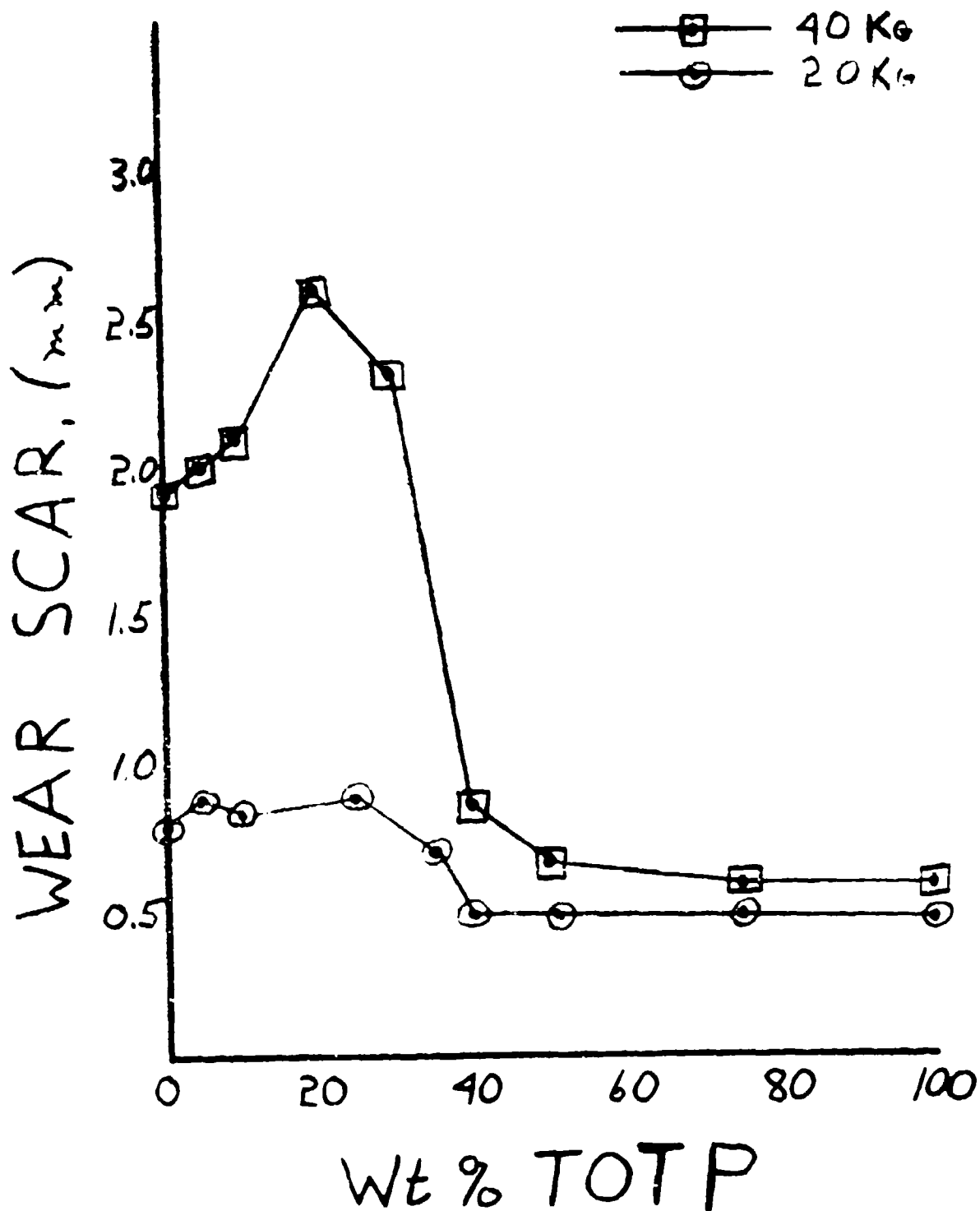


Figure 7. Four-Ball Wear Test Results on Dimethyl Siloxane Fluid (50 cs) with TOTP at 20 and 40 Kg Load

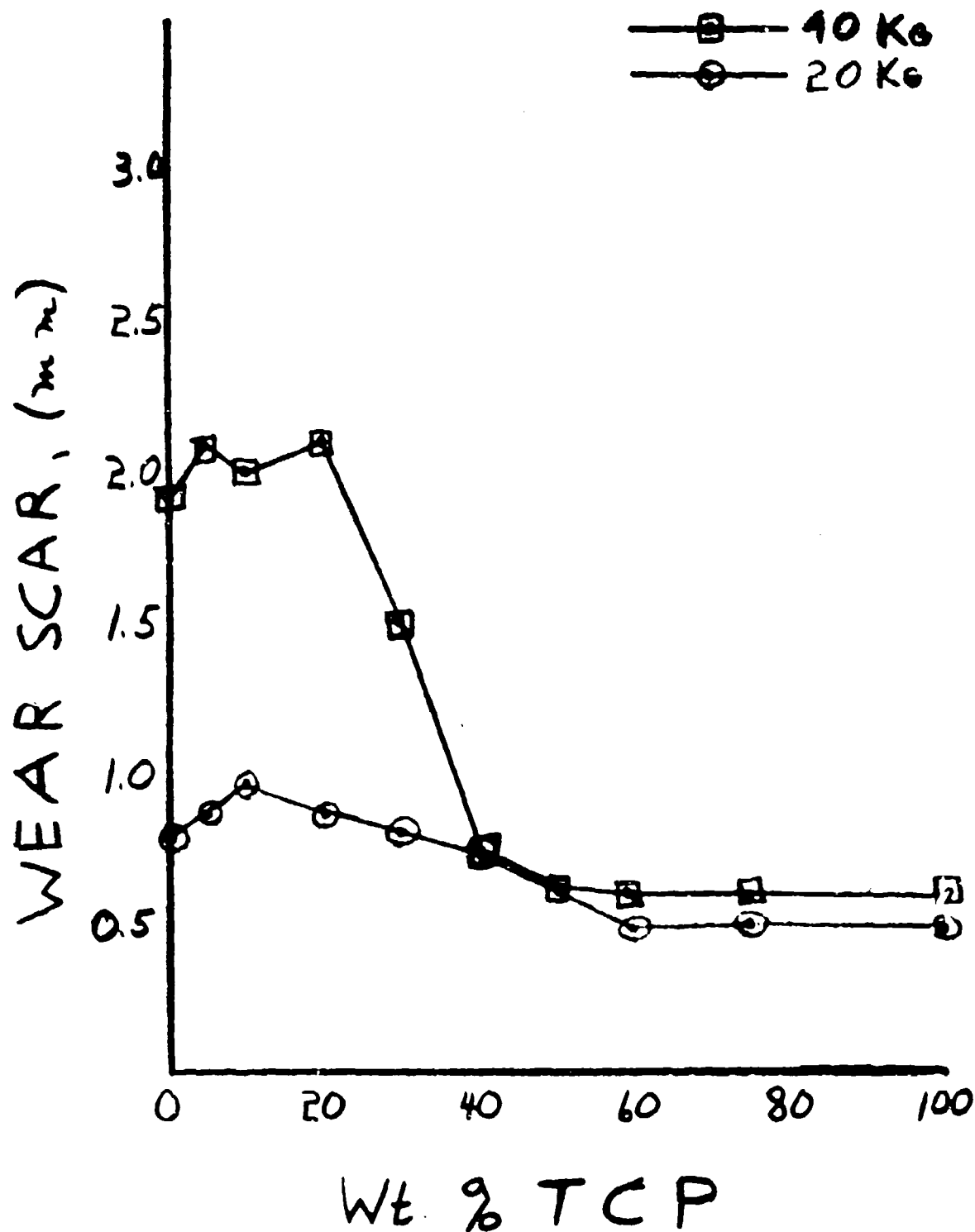


Figure 8. Four-Ball Wear Test Results on Dimethyl Siloxane Fluid (50 cs) with TCP at 20 and 40 Kg Load

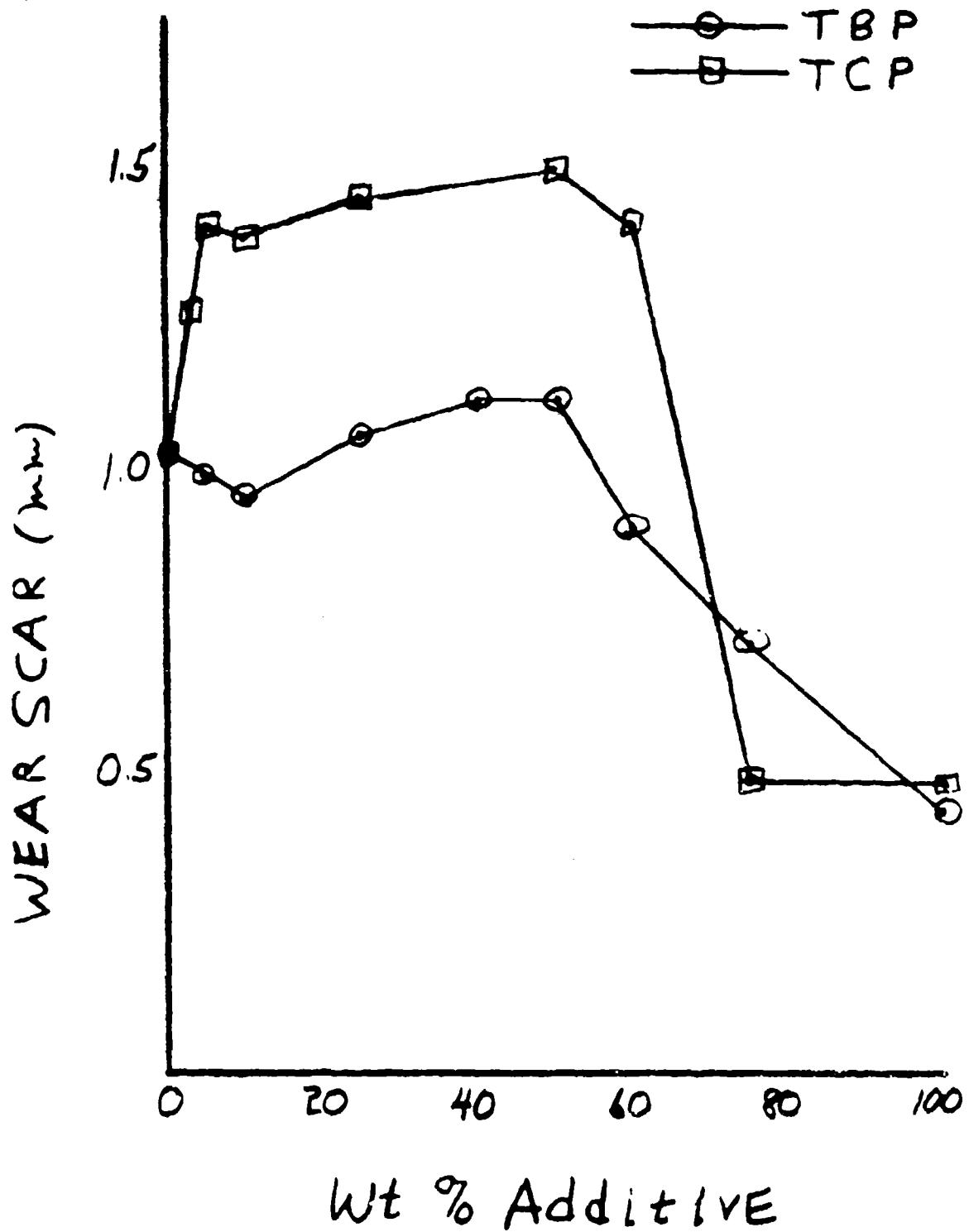


Figure 9. Four-Ball Wear Test Results on Dimethyl Siloxane Fluid (10 cs) with TBP and TCP at 20 Kg Load

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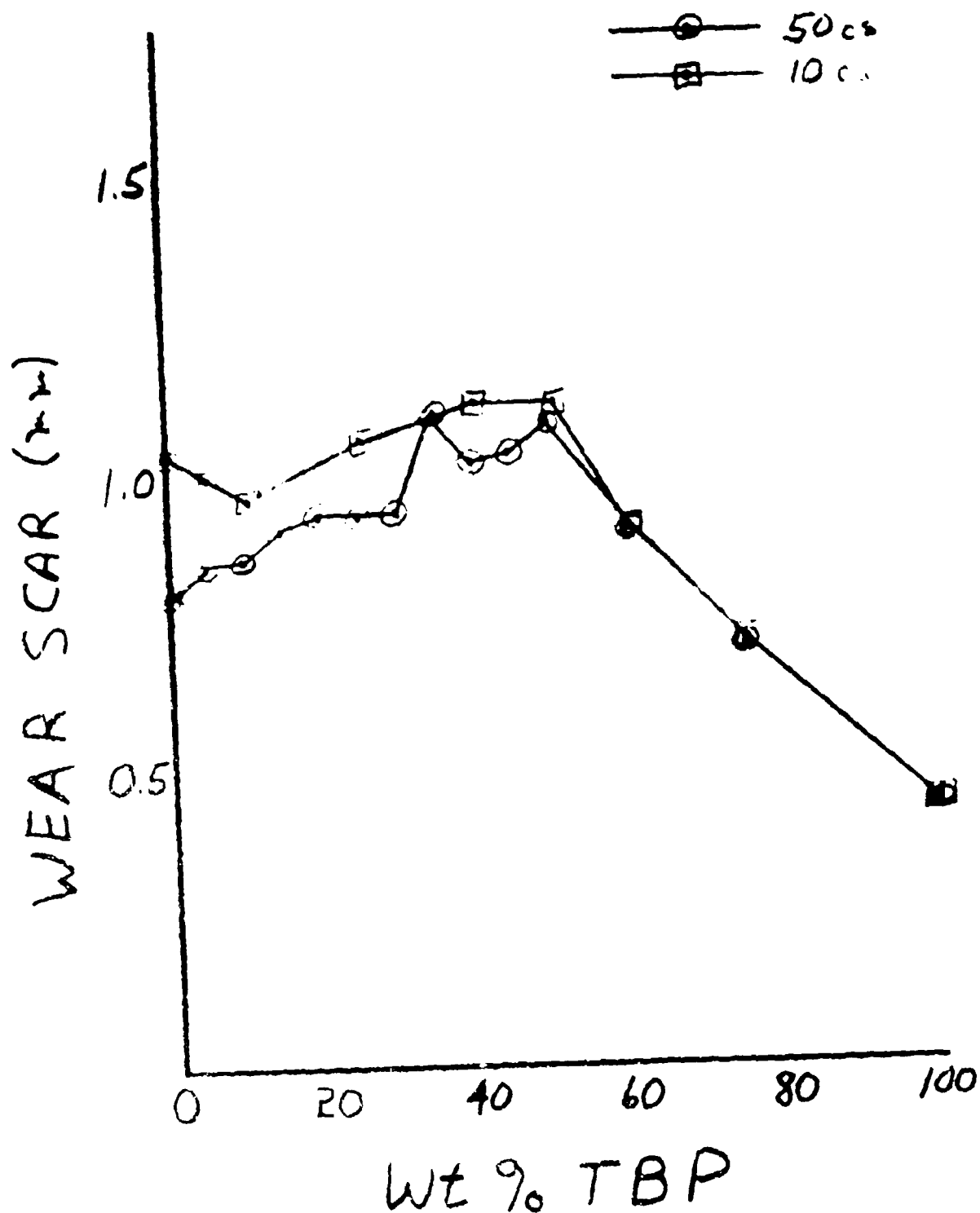


Figure 10. Four-Ball Wear Test Results on Dimethyl Siloxane Fluids (10 and 50 cs) with TBP at 20 Kg Load

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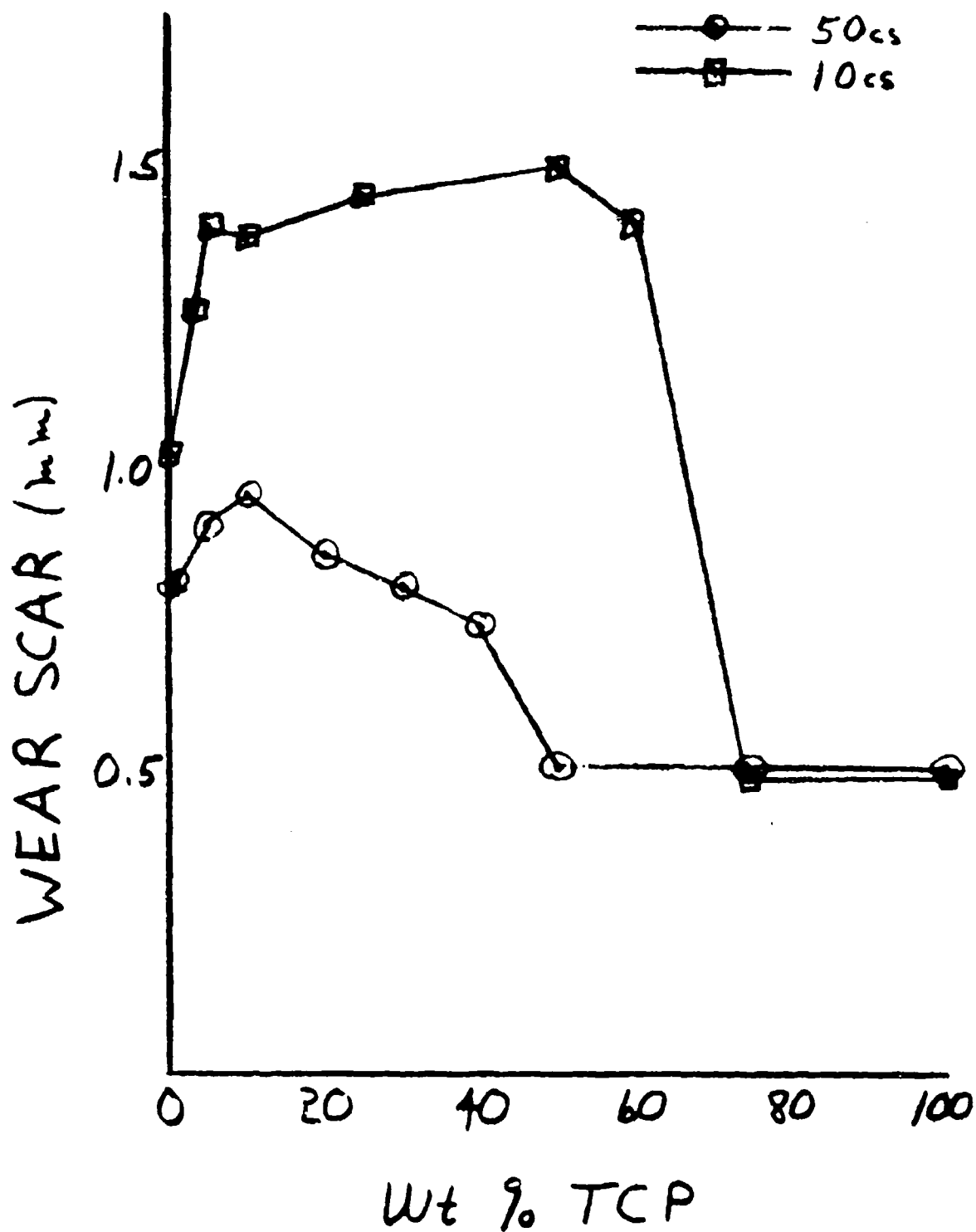


Figure 11. Four-Ball Wear Test Results on Dimethyl Siloxane Fluids (10 and 50 cs) with TCP at 20 Kg Load

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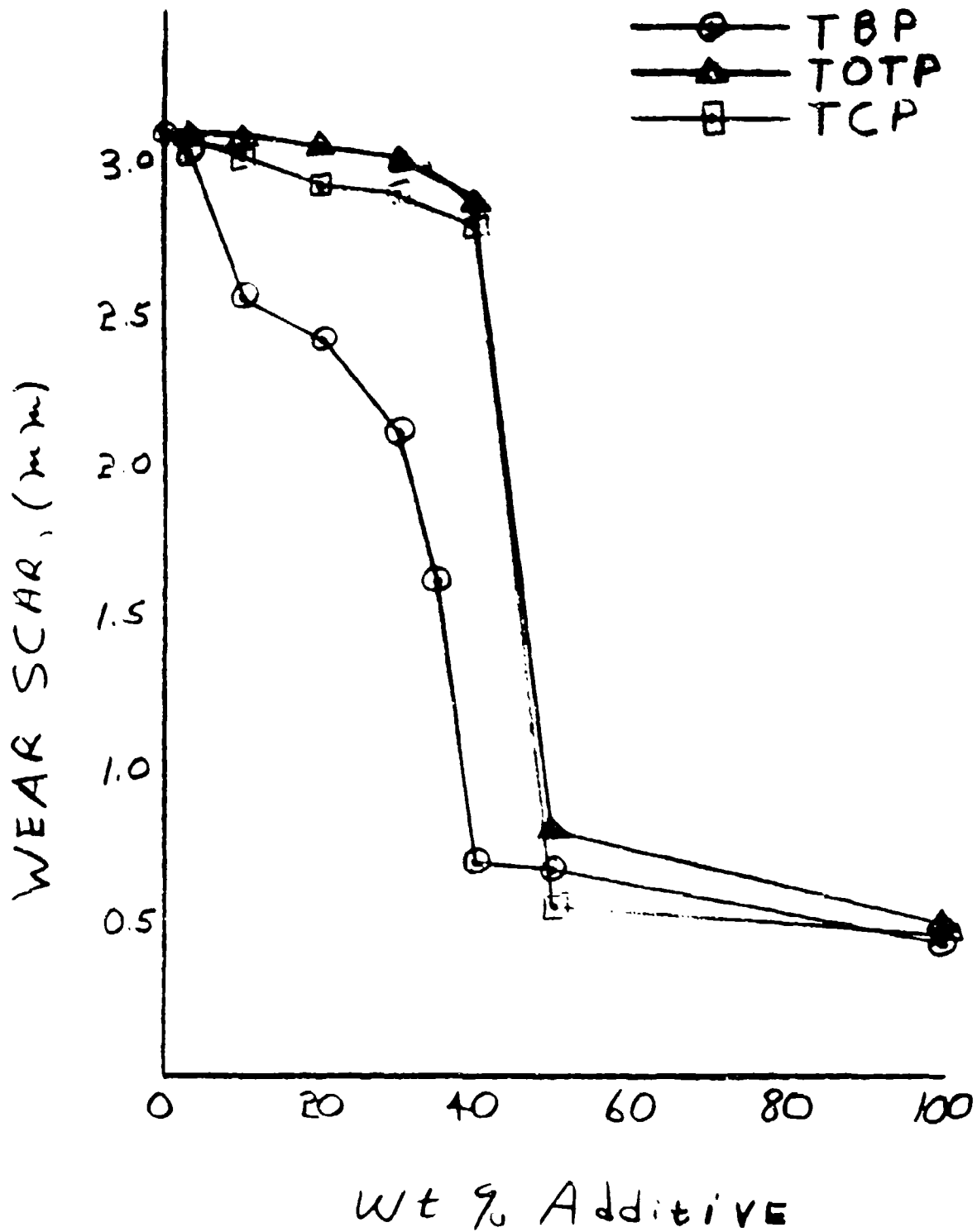


Figure 12. Four-Ball Wear Test Results on Phenylmethyl Siloxane Fluid with TBP, TOTP and TCP at 20 Kg Load

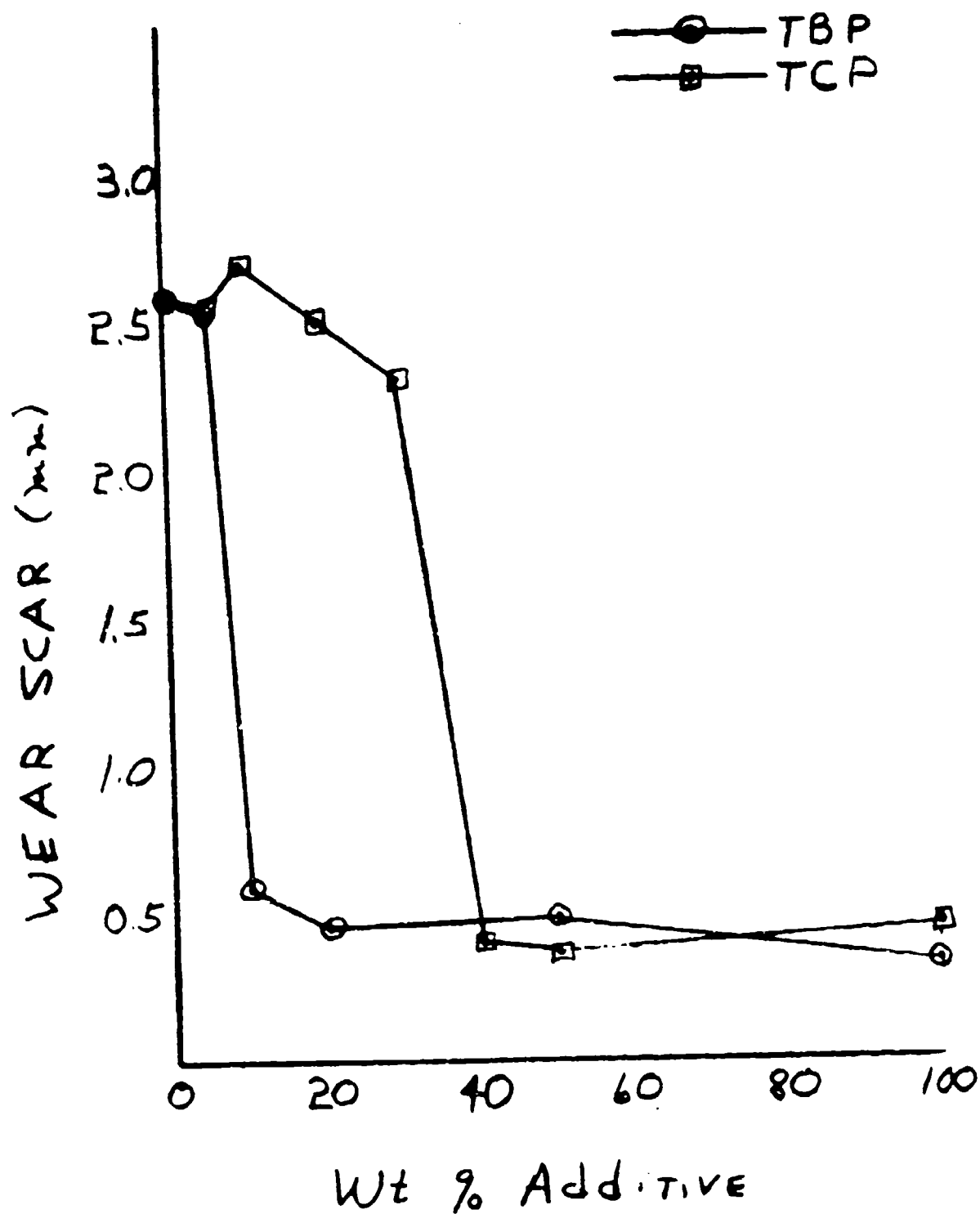


Figure 13. Four-Ball Wear Test on Phenylmethyl Siloxane Fluid with TBP and TCP at 10 Kg Load

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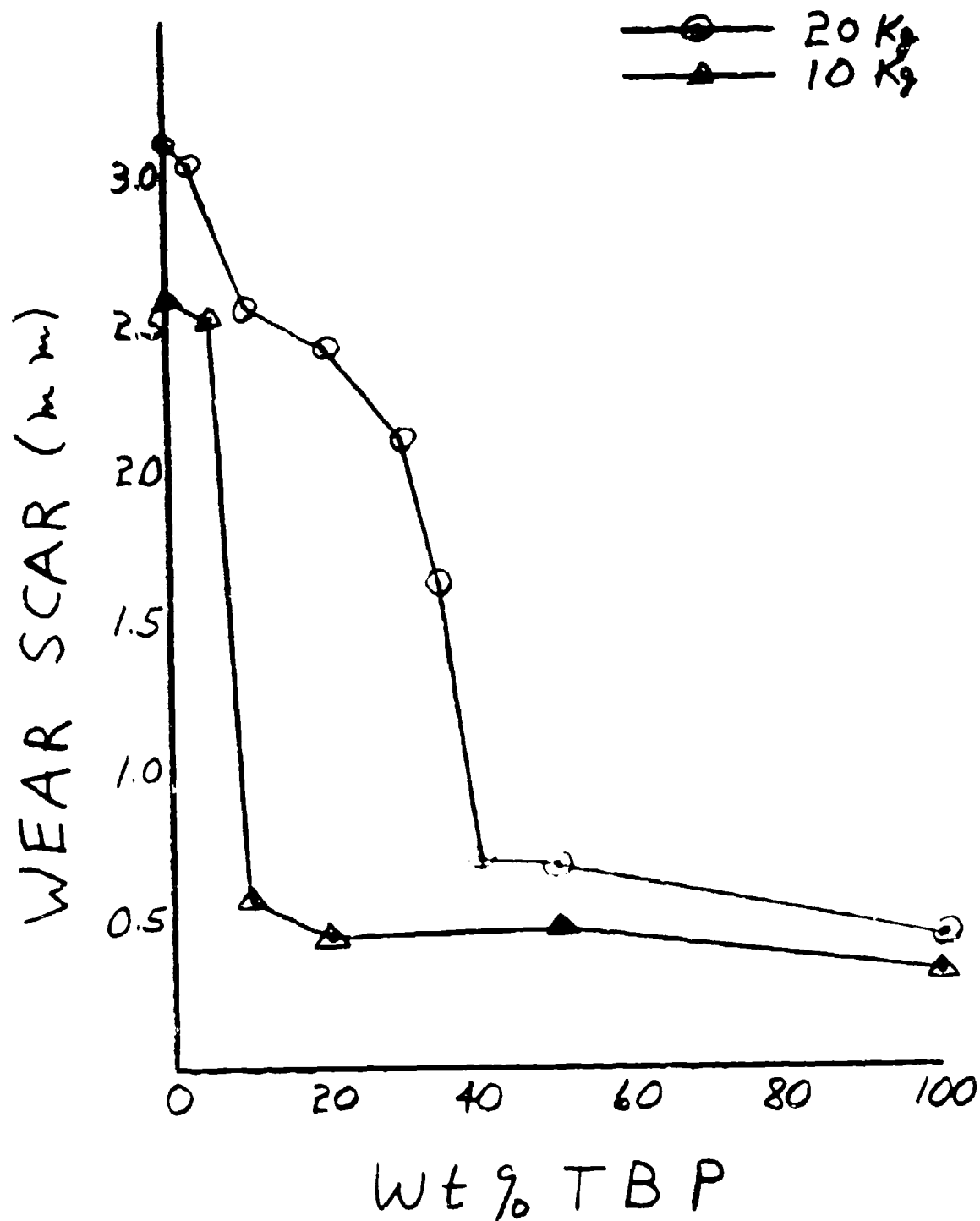


Figure 14. Four-Ball Wear Test Results on Phenylmethyl Siloxane Fluid with TBP at 10 and 20 Kg Load

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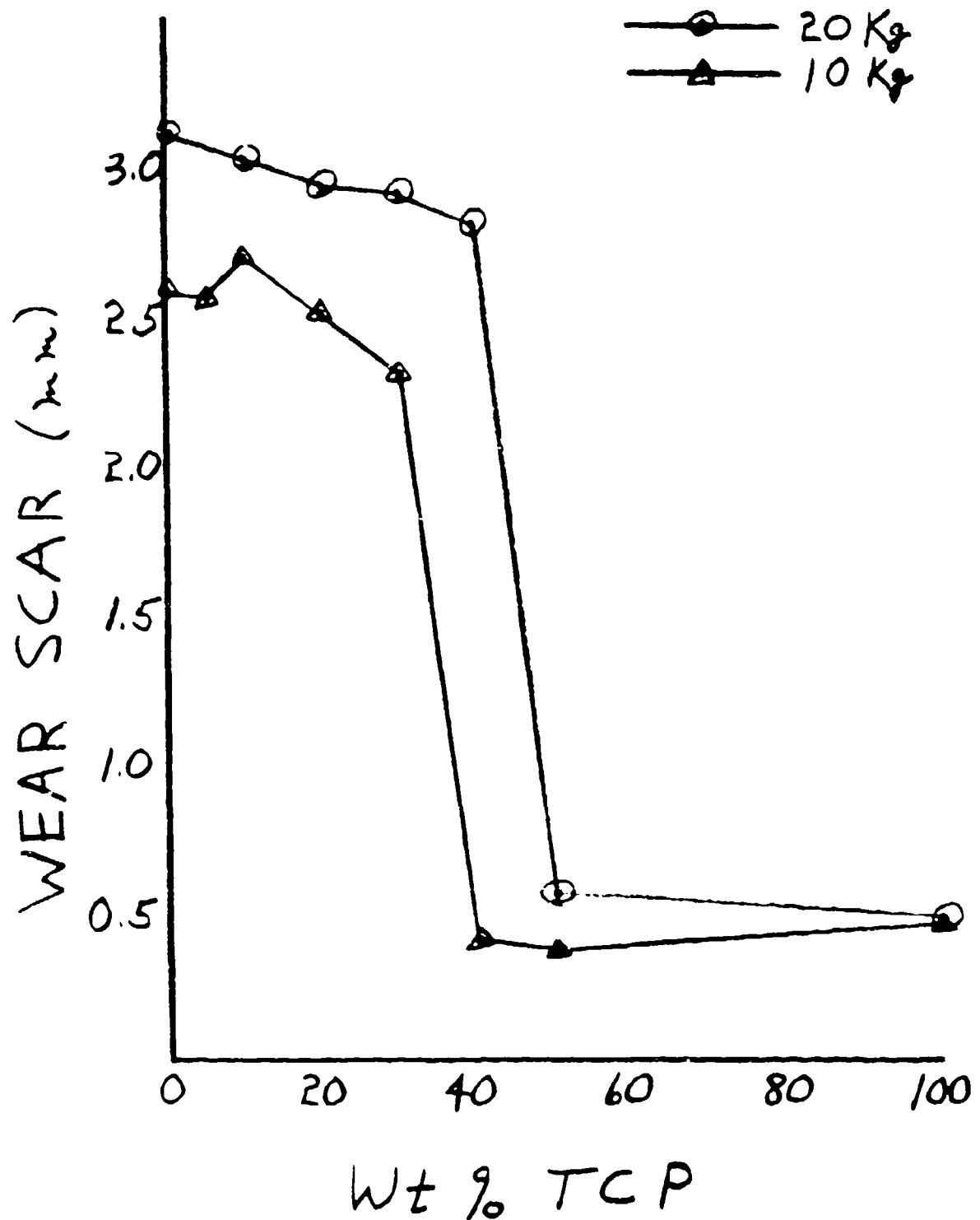


Figure 15. Four-Ball Wear Test Results on Phenylmethyl Siloxane Fluid with TCP at 10 and 20 Kg Load

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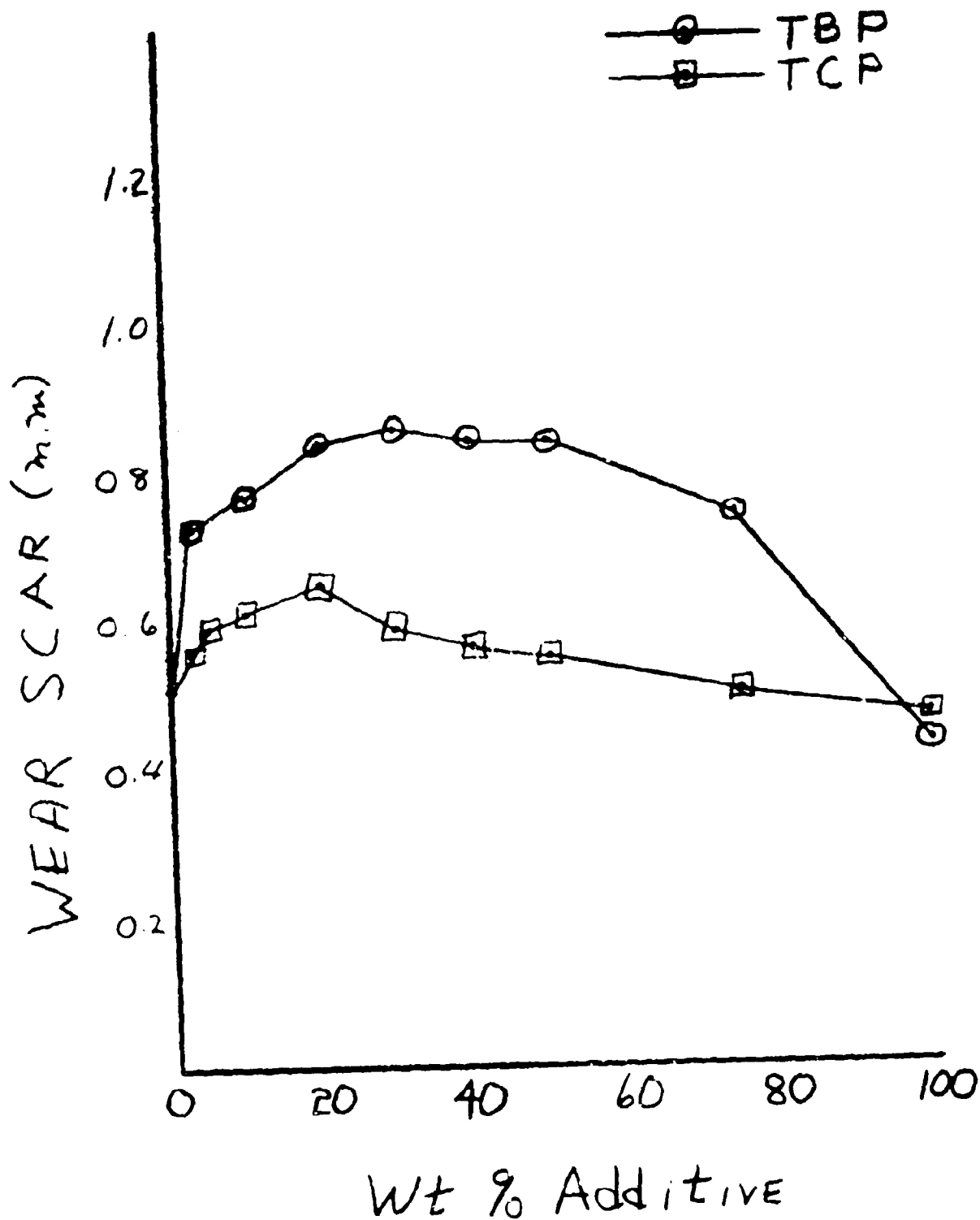


Figure 16. Four-Ball Wear Test Results on Dichlorophenylmethyl Siloxane Fluid with TBP and TCP at 20 Kg Load

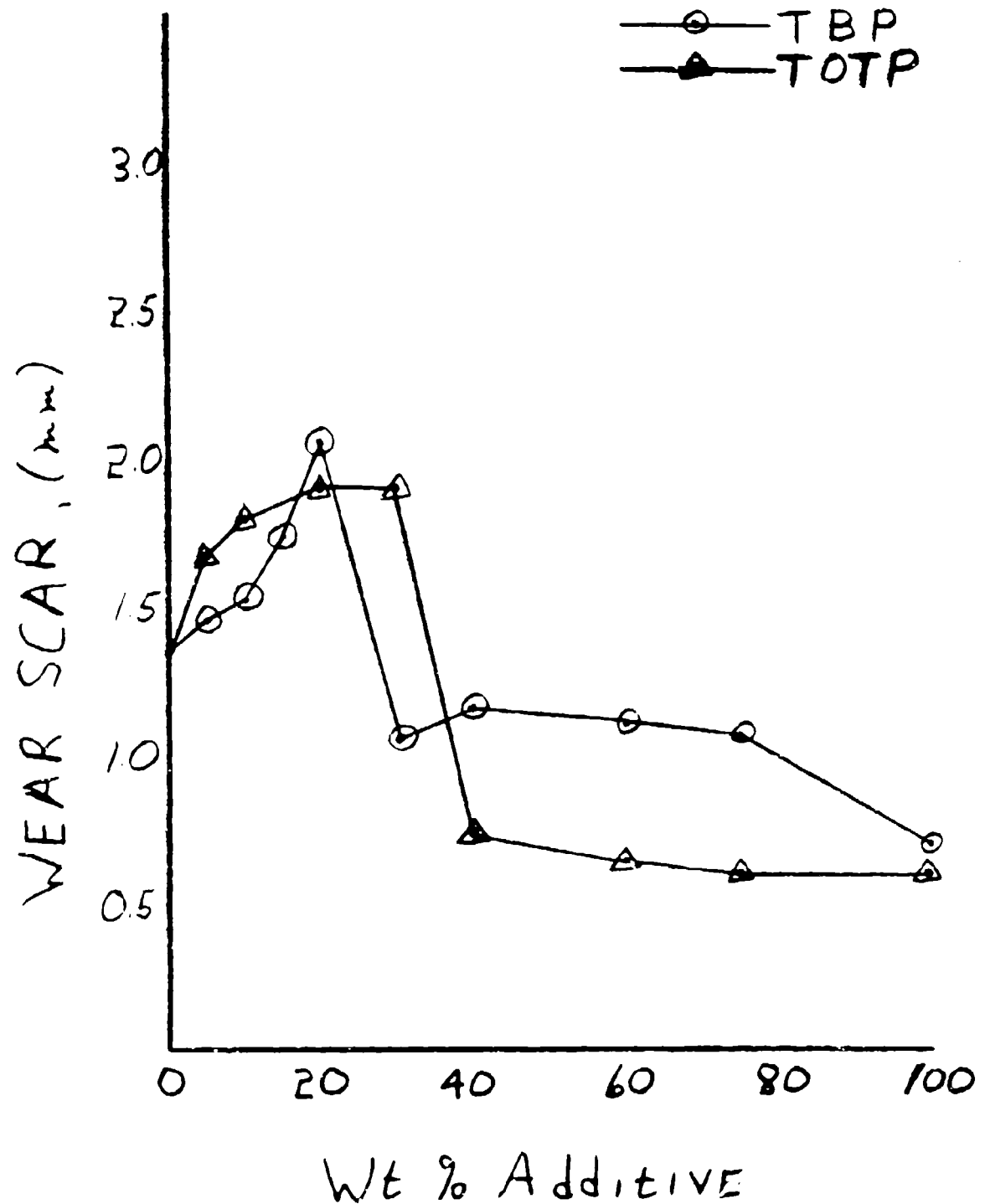


Figure 17. Four-Ball Wear Test Results on Dichlorophenylmethyl Siloxane Fluid with TBP and TOTP at 40 Kg Load

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—○— TBP
—△— TOTP

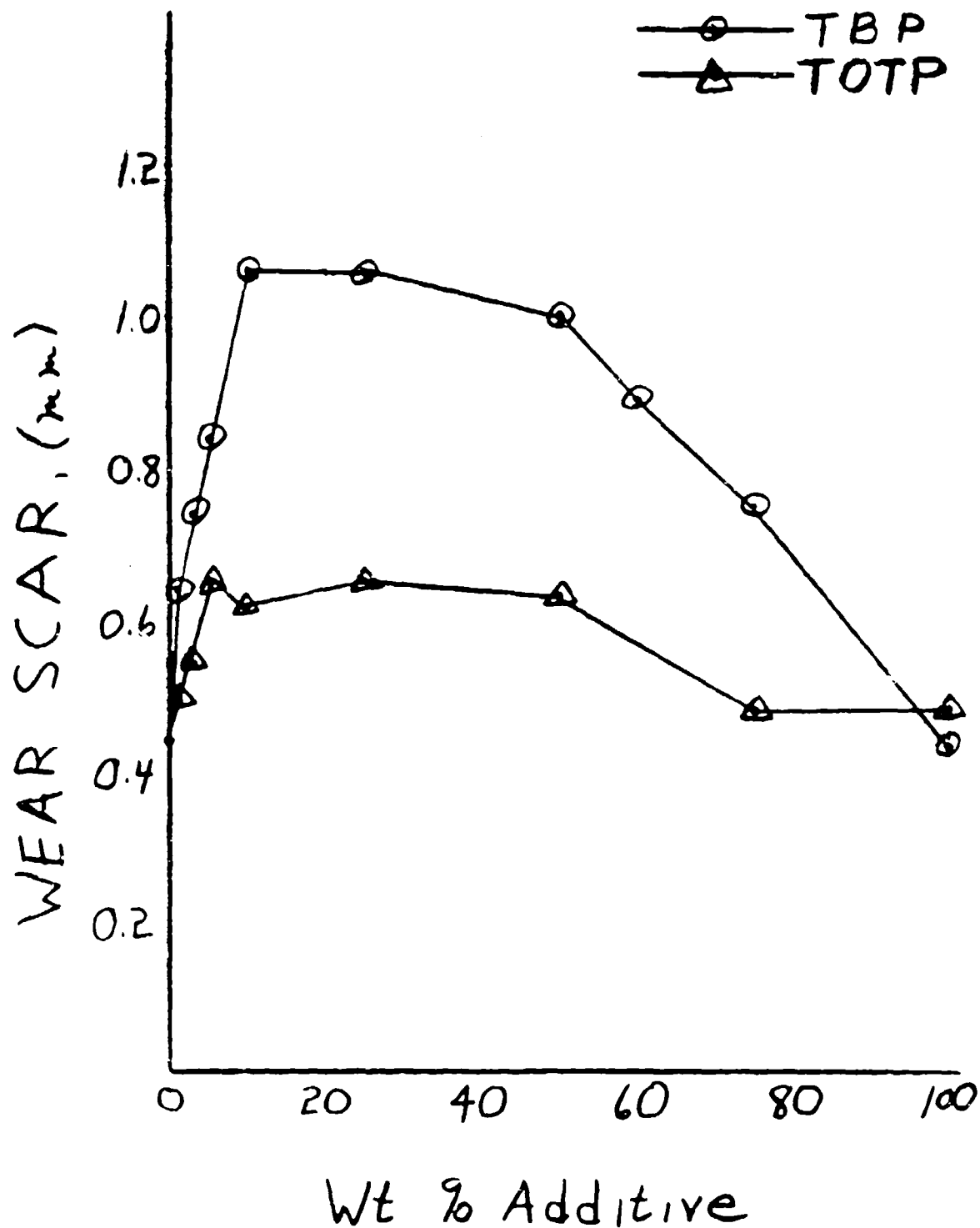


Figure 18. Four-Ball Wear Test Results on Tetrachlorophenylmethyl Siloxane Fluid with TBP and TOTP at 20 Kg Load

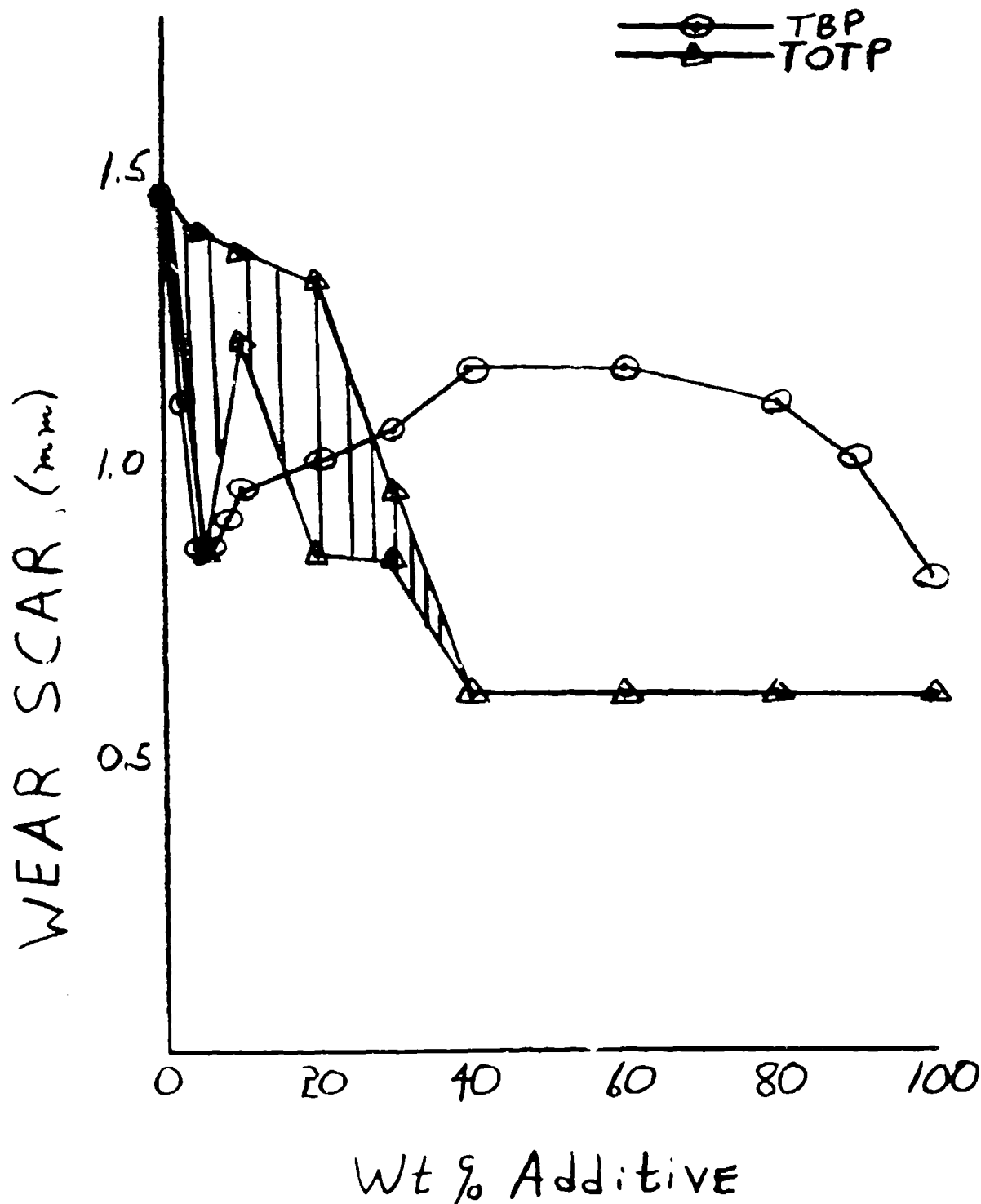


Figure 19. Four-Ball Wear Test Results on Tetrachlorophenylmethyl Siloxane Fluid with TBP and TOTP at 40 Kg Load

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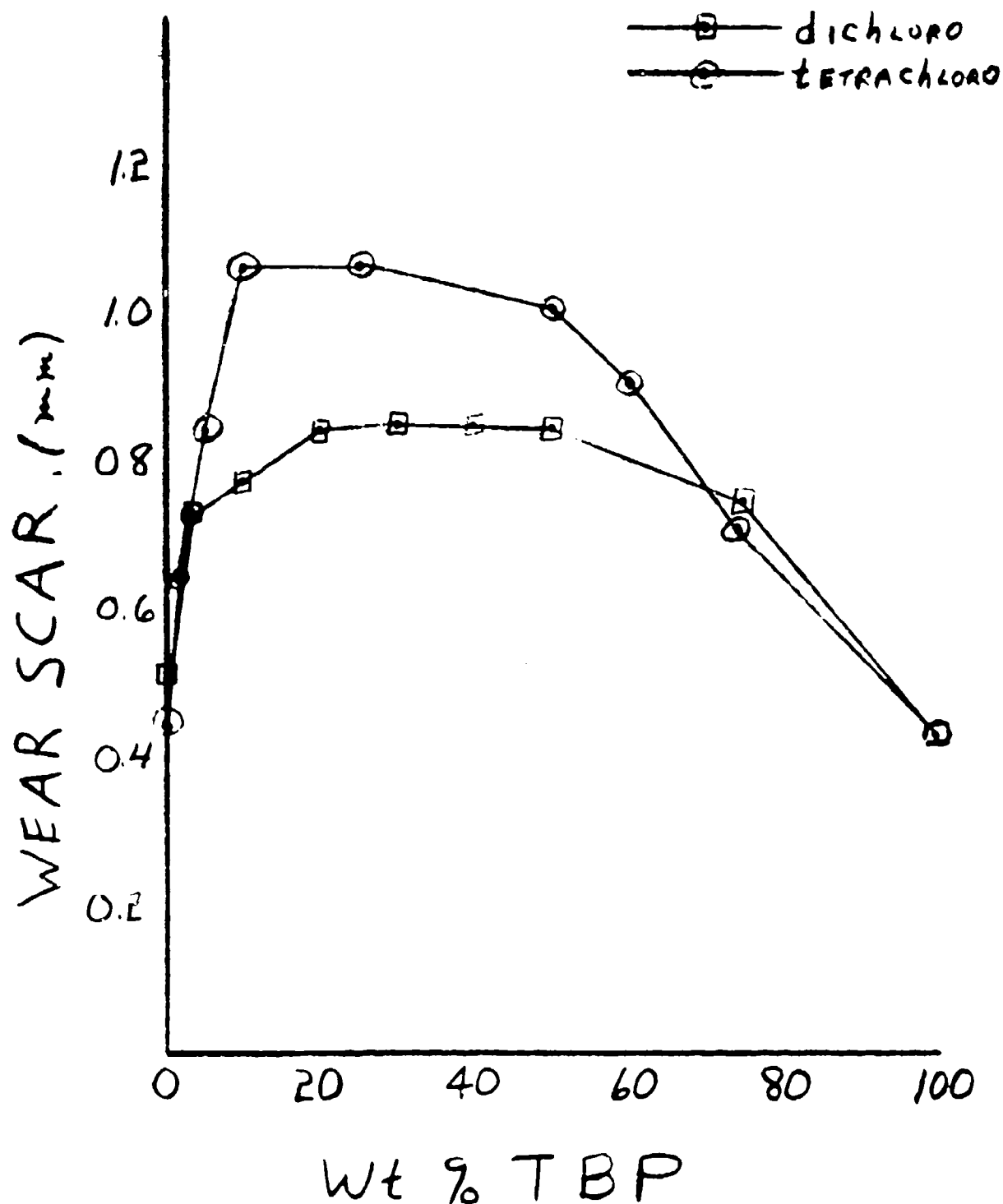


Figure 20. Four-Ball Wear Test Results on Dichlorophenylmethyl and Tetrachlorophenylmethyl Siloxane Fluids with TBP at 20 Kg Load

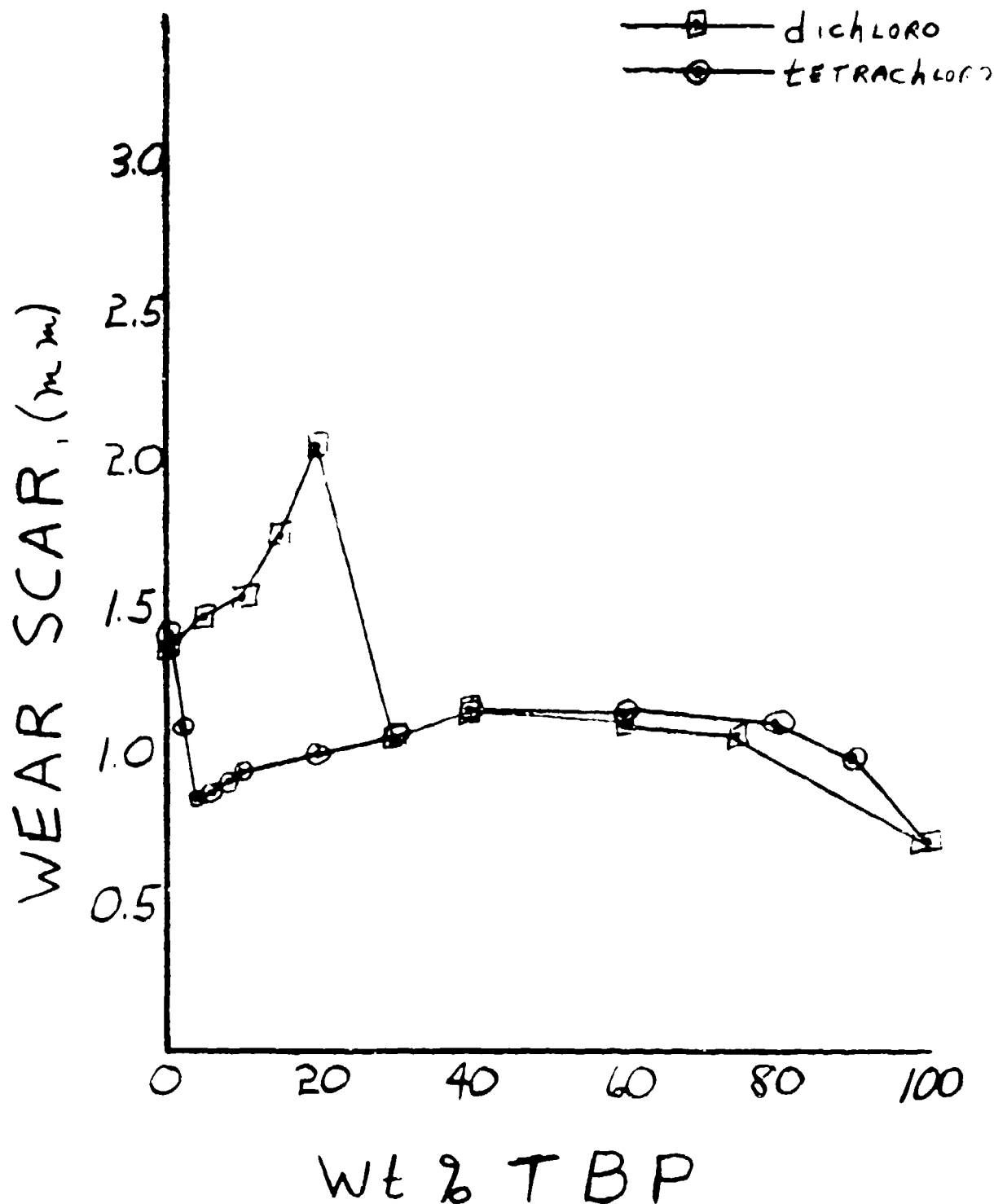


Figure 21. Four-Ball Wear Test Results on Dichlorophenylmethyl and Tetrachlorophenylmethyl Siloxane Fluids with TBP at 40 Kg Load

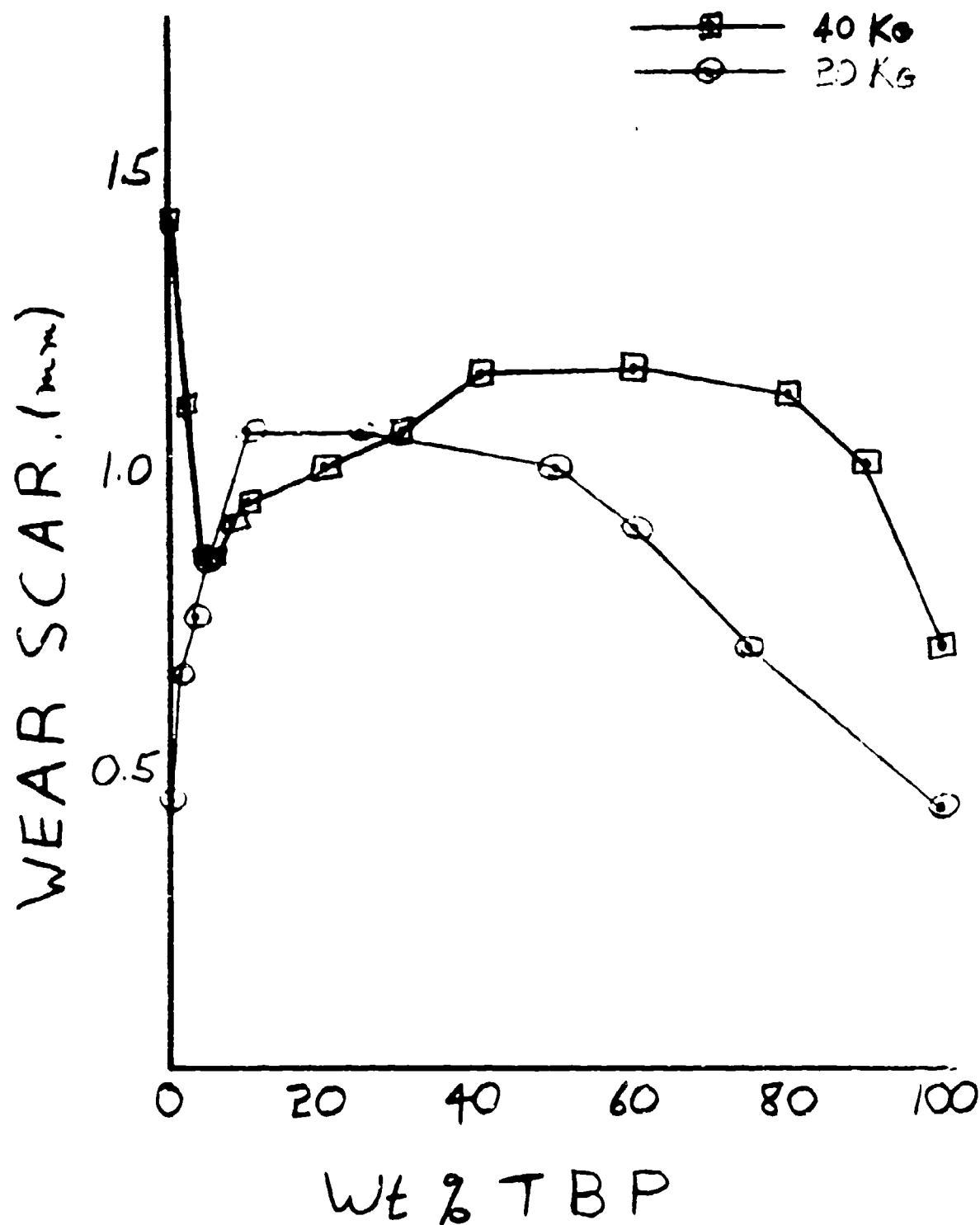


Figure 22. Four-Ball Wear Test Results on Tetrachlorophenylmethyl Siloxane Fluid with TBP at 20 and 40 Kg Load

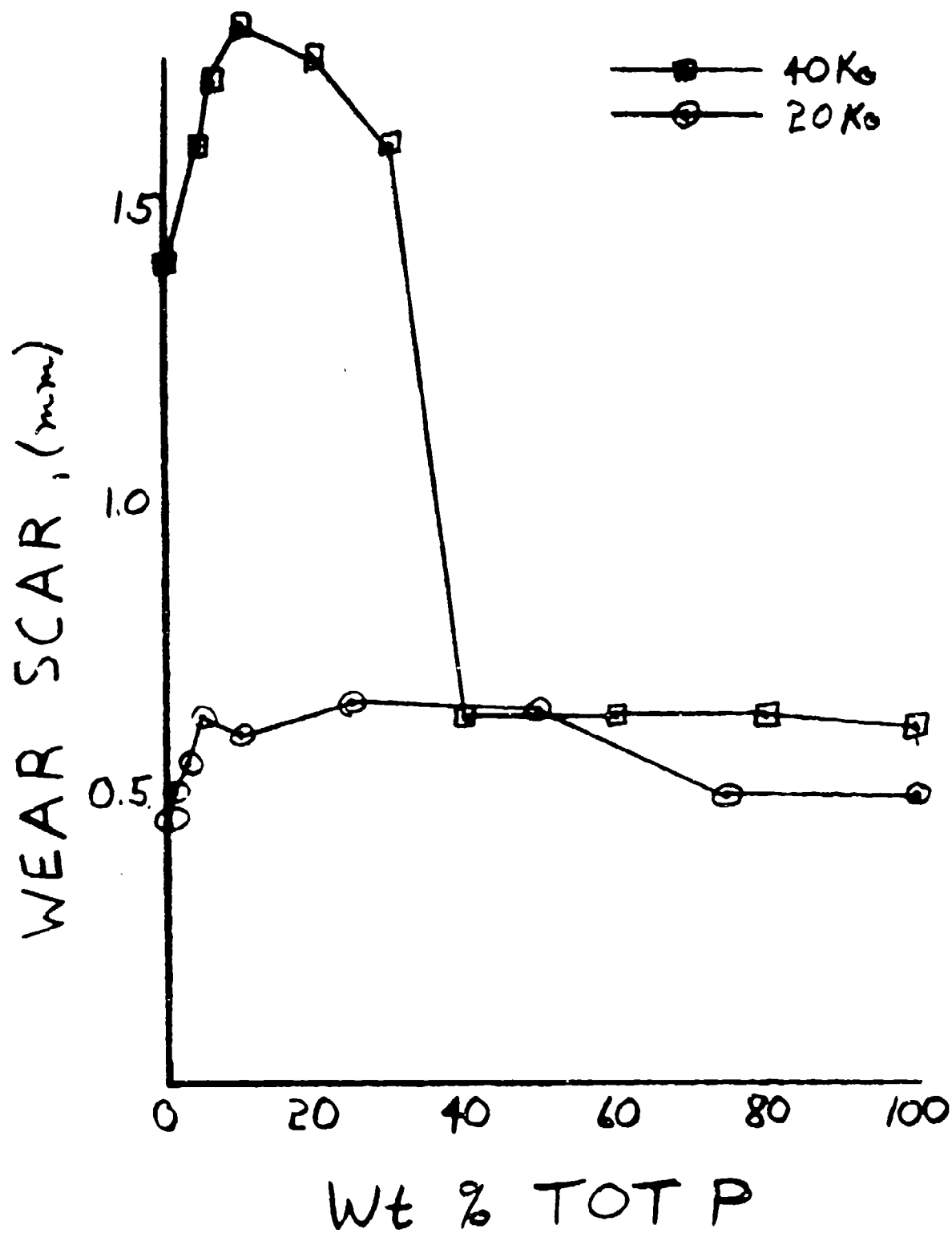


Figure 23. Four-Ball Wear Test Results on Tetrachlorophenylmethyl Siloxane Fluid with TOT P at 20 and 40 Kg Load

TABLE 1. FOUR-BALL WEAR TEST RESULTS ON TETRACHLOROPHENYLMETHYL
SILOXANE FORMULATIONS AT 167°F, 40 Kg LOAD

<u>Formulation No.</u>	<u>Chlorendate (wt. %)</u>	<u>Thiadiazole (wt. %)</u>	<u>Wear Scar Diameter (mm)</u>
1	0	0	1.30
2	0	0.25	0.82
3	0	0.50	0.83
4	0	1.0	0.97
5	1.0	0	0.93
6	2.0	0	0.77
7	3.0	0	0.80
8	4.0	0	0.79
9	5.0	0	0.95
10	1.0	0.25	0.72
11	2.0	0.25	0.62
12	3.0	0.25	0.69
13	5.0	0.25	0.79
14	2.0	0.40	0.74
15	5.0	0.50	0.80
16	5.0	1.00	0.81
17	2.0	0.10	0.67

TABLE II. FOUR-BALL WEAR TEST RESULTS ON COMPARISON FLUIDS AT 167°F, 40 Kg
LOAD

<u>Designation</u>	<u>Base Fluid</u>	<u>Wear Scar Diameter (mm)</u>
Formulation II	Silicone	0.62
MIL-H-5606	Petroleum	0.65
MIL-H-83282	Synthetic Hydrocarbon	0.55
MIL-H-19457	Phosphate Ester	0.54

TABLE III. FOUR-BALL WEAR TEST RESULTS ON TETRACHLOROPHENYLMETHYL SILOXANE FORMULATIONS AT TWO TEMPERATURES (40 Kg LOAD)

<u>Formulation No.</u>	<u>Wear Scar Diameter (mm)</u>	
	<u>167°F</u>	<u>350°F</u>
1	1.30	*
3	0.83	0.95
6	0.77	1.39
11	0.62	0.68

* Indicates that the test could not be completed because of excessive wear.

TABLE IV. COMPARISON OF ANTIWEAR PROPERTIES OF VARIOUS PHOSPHATE ADDITIVES IN DIMETHYL SILOXANE (50 cs) AT 20 Kg LOAD

<u>Phosphate</u>	Moles of Additive, per 1000 g Siloxane		
	<u>At Maximum Wear Scar</u>	<u>To Reduce Wear Scar to Same as 100% Siloxane</u>	<u>To Reduce Wear Scar to Same as 100% Additive</u>
TOP	0.58 (1.08)	0.99 (0.77)	6.9 (0.31)
TBP	2.0-3.8 (1.10)	8.8 (0.77)	11.3 (0.43)
TOTOP	0.91 (0.87)	1.2 (0.77)	1.8 (0.48)
TCP	0.30 (0.96)	1.2 (0.77)	2.7 (0.47)

Note: Numbers in parenthesis refer to the wear scar diameter in millimeters at the given concentration.

TABLE V. COMPARISON OF ANTIWEAR PROPERTIES OF VARIOUS PHOSPHATE ADDITIVES IN DIMETHYL SILOXANE (50 cs) AT 40 Kg LOAD

<u>Phosphate</u>	Moles of Additive, per 1000 g Siloxane		
	<u>At Maximum Wear Scar</u>	<u>To Reduce Wear Scar to Same as 100% Siloxane</u>	<u>To Reduce Wear Scar to Same as 100% Additive</u>
TOP	1.5 (2.41)	1.8 (1.90)	6.9 (0.51)
TBP	2.5 (2.37)	3.0 (1.90)	> 11.3 (0.69)
TOTP	0.68 (2.59)	1.3 (1.90)	2.7 (0.58)
TCP	0.68 (2.09)	0.81 (1.90)	2.7 (0.58)

Note: Numbers in parenthesis refer to wear scar diameter in millimeters at the given concentration.

TABLE VI. FOUR-BALL WEAR TEST RESULTS ON POLYSILOXANE BASE FLUIDS AT 167°F

Polysiloxane	Viscosity at 77°F (cs)	Wear Scar (mm)		
		10 Kg	20Kg	40 Kg
Dimethyl	100	0.45	0.65	1.75
Dimethyl	50	0.45	0.77	1.90
Dimethyl	10	0.68	1.02	*
Phenylmethyl	75	2.58	3.12	*
Dichlorophenylmethyl	75	-	0.51	1.35
Tetrachlorophenylmethyl	75	-	0.44	1.41

* Indicates test could not be completed because of excessive wear.

TABLE VII. COMPARISON OF ANTIWEAR PROPERTIES OF VARIOUS PHOSPHATE ADDITIVES IN PHENYLMETHYL SILOXANE FLUID

<u>Phosphate</u>	<u>Load Kg</u>	<u>Moles to Additive per 1000 g Siloxane at sharp "break point" in wear curve</u>
TBP	10	0.20 (2.52)
	20	No sharp break point.
TCP	10	1.16 (2.31)
	20	1.81 (2.81)

Note: Numbers in parenthesis refer to the wear scar diameter at the given concentration in millimeters.

TABLE VIII. COMPARISON OF ANTIWEAR PROPERTIES OF VARIOUS PHOSPHATE ADDITIVES
IN CHLOROPHENYLMETHYL SILOXANE FLUIDS AT 40 Kg LOAD

<u>Phosphate</u>	<u>wt. %</u>	<u>Wear Scar Diameter (mm)</u>	
		<u>dichloro</u>	<u>tetrachloro</u>
None	-	1.35	1.41
TBP	5	1.46	0.86
TOP	5	1.67	0.77
TEP*	10	1.62	0.81

*Triethyl phosphate